Susceptibility of Diluted Bitumen Products from the Alberta Tar Sands to Sinking in Water

by

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Executive Summary

Proposed shipment of diluted bitumen products derived from the Alberta tar sands has raised concerns regarding their propensity to sink in receiving waters following accidental discharges. I review here the results of three publicly available studies that contain data relevant to evaluating the ambient temperatures and salinities under which these products might sink. Specifically, I compare the density of the bitumen products studied as a function of temperature and weathering with the density of water as a function of temperature and salinity, to identify conditions where the density of bitumen products could exceed the density of receiving waters and hence sink. I then compare these results with ambient environmental conditions in the confined channel assessment area that extends from Kitimat, British Columbia to the outer coast, to show that at least some diluted bitumen products would be expected to sink in fresh and in brackish marine waters less than 24 h following an accidental discharge.

My results show that conclusions based on previous studies of the effects of weathering on the density of diluted bitumen products fail to consider the differential effects of temperature on bitumen products in comparison with fresh and marine waters. Conclusions based on experiments conducted at 15 °C are not necessarily valid at lower temperatures, because the density of bitumen products increases faster with declining temperatures than does the density of fresh or marine waters. Consequently, weathered bitumen products that float at 15 °C may sink at 5 °C.

The experiments conducted to evaluate the effects of weathering on densities of diluted bitumen products (Belore 2010, SL Ross 2012) correspond to ambient environmental conditions in the confined channel assessment area that are among the least conducive to weathering. This is primarily because:

1. The thickness of the diluted bitumen product tested in one of the studies (2 cm; Belore 2010) was much thicker than would be encountered following initial release into the environment (< ~1 mm), and

2. The experimental wind speeds (1.5 - 3 m/s) were below the average wind speeds of the confined channel assessment area, where average wind speeds are higher (~5 m/s) and on windy days are considerably higher (~15 m/s). Because wind speed is a major factor affecting weathering rates, it may overcome effects of temperature differences in the range of 0 - 15 °C typically present in the confined channel assessment area.

Consequently, the results of the most environmentally realistic tests attempted to date to simulate weathering rates of diluted bitumen products nonetheless understate likely weathering rates in the field.

Because the effects of weathering on the density of only a very few bitumen products have been evaluated experimentally, it is plausible that other products that might be shipped through the proposed Northern Gateway pipeline might be even more susceptible to sinking following accidental discharges. Additional and more careful studies are needed to address this question.

Introduction

The enormous volume of bitumen products likely to be transported through the proposed Northern Gateway pipeline (NGP) naturally prompts concerns about accidental spills. The proposed NGP would facilitate transport of bitumen products from Bruderhiem near Edmonton, AB to a proposed marine oil trans-shipment terminal at Kitimat, BC, where product would be loaded onto oil tankers. Accidental spills may occur on land from pipeline ruptures, where oil may flow into freshwater bodies, or at sea from tankers outbound from the proposed terminal. Once discharged into water bodies, the oil may cause considerable environmental damage, including damage to aquatic resources. Such damage is far more difficult to evaluate and to remediate if the oil sinks following discharge to receiving waters.

Anticipating the environmental effects of oil spills involving products derived from the Alberta tar sands requires particular care because of their unusual characteristics. Unlike typical crude oils, the geological processes that led to formation of the tar sands promoted losses of the lower molecular weight components through volatilization as well as extensive biodegradation (National Energy Board 2000). An important consequence of the essentially "pre-weathered" nature of the resulting bitumen is that conclusions regarding fate based on experience with or scientific study of typical crude oils must be made with extraordinary caution.

In particular, ordinarily crude oils and most petroleum products derived from them are considerably less dense than water and so are not usually prone to sinking in water. But densities of at least some of the bitumen products from the Alberta tar sands are inherently greater than that of water, so they are prone to sinking unless diluted with lower-density solvents. The behaviour of the diluted products once released to the environment thus depends in substantial part on the particular characteristics of the diluent. According to the proposed shipment tariff, such dilution would be mandatory to reduce the density of the diluted bitumen to less than 940 kg/m^3, well below the threshold for sinking in water (~1,000 kg/m^3). However, volatilization or dissolution of the lower-density solvent after an accidental discharge into the environment would increase the density of the remaining material, possibly to values causing it to sink.

My objective here is to evaluate how evaporative weathering and temperature affect how diluted bitumen products from the Alberta tar sands interact physically with potential receiving waters with regard to transport and sinking.

Theory

When mixed, the force of gravity causes the denser of two immiscible liquids to sink. Identifying which liquid sinks is usually a simple matter of measuring the densities, but more care is needed as the densities approach equivalence. At constant pressure, differences in the variation of density with temperature may result in different ordering at different temperatures, with the liquid that floats at a high temperature becoming the one that sinks at a lower temperature. Predicting results at a specified temperature then requires careful comparison of the temperature dependencies of the liquids involved.

The density variation of pure water with temperature ($\rho_w(T)$, where T is in °C) can be calculated to an accuracy of about 30 g/m^3 as:

$$\rho_w(T) = 999.842594 + 0.6793952\,T - 9.09529\text{x}10^{-3}\,T^2 + 1.001685\text{x}10^{-4}\,T^3 - 1.120083\text{x}10^{-6}\,T^4 + 6.536332\text{x}10^{-9}\,T^5 \quad \text{eq 1}$$

Equation 1 generates the internationally-accepted density values for Standard Mean Ocean Water at zero salinity (SMOW; Millero & Poisson 1981, UNESCO 1981), which is essentially fresh water that has the same isotopic composition as seawater. Densities of water from eq 1 range from 998.206 kg/m^3 at 20 °C to a maximum of 999.975 at 3.98 °C, declining to 999.843 kg/m^3 at 0 °C.

The density of seawater (ρ_{sw}) depends strongly on salinity as well as temperature, which may be calculated as:

$$\rho_{sw}(T,S) = \rho_w + (0.824493 - 4.0899\text{x}10^{-3}\,T + 7.6438 \text{ x } 10^{-5}\,T^2 - 8.2467\text{x}10^{-7}\,T^3 + 5.3875\text{x}10^{-9}\,T^4)\,S + (-5.5.72466\text{x}10^{-3} + 1.0227\text{x}10^{-4}\,T - 1.6546\text{x}10^{-6}\,T^2)S^{3/2} + 4.8314\text{x}10^{-4}\,S^2 \quad \text{eq 2}$$

Equation 2 defines the International One Atmosphere Equation of State of Seawater, 1980, and provides density values for seawater in the range of -2 to 40 °C and 0 - 42 practical salinity units (psu, denoted here as ‰) at one standard atmosphere pressure.

For materials like bitumen products from the Alberta tar sands that are less well characterized than fresh water or seawater, an equation for the density variation with temperature may be calculated from measurements of density and information on the coefficient of thermal expansion. The coefficient of thermal expansion, β, is the proportional change of volume with a change in temperature:

$$\beta = \frac{1}{V}\frac{dV}{dT} \qquad \text{eq 3}$$

Assuming β is constant over small temperature ranges, equation 3 may be integrated directly to give the following expression relating the volume $V(T)$ of a fixed mass of material at some temperature T to an initial reference volume V' and temperature T':

$$V(T) = V' \exp\,(\beta \Delta T) \qquad \text{eq 4}$$

where $\Delta T = T - T'$. Recognizing that density is the ratio of a fixed mass of material to its temperature-dependent volume, the density variation of bitumen products with temperature, $\rho_b(T)$ may be expressed as:

$$\rho_b(T) = \rho_b' /\exp(\beta \Delta T) \qquad \text{eq 5}$$

where ρ_b' is the density of the product at the reference temperature T'. Equation 5 may be used to formulate a precise criterion for determining whether bitumen products will sink over a specified temperature range ΔT in water of salinity S: if $\rho_b(T) > \rho_{sw}(T,S)$, then the bitumen product will sink.

In the next section, I use the results of experimental measurements to develop explicit versions of eq 5 for determining the variation of density with temperature for bitumen samples from the Alberta tar sands, and then I compare these results with the density of fresh water and seawater using eqs 1 and 2.

Effects of Temperature and Weathering on the Density of Diluted Alberta Tar Sands Bitumen Products

There have been just three publicly available studies that present enough detail on the density of bitumen samples from the Alberta tar sands to develop a quantitative relation of density dependence on temperature using equation 5. These studies provide data on bitumen samples from four different sources and, from the density data presented, coefficients of thermal expansion (β) can be calculated.

Environment Canada performed extensive measurements on the chemical composition and on physical data at two temperatures and weathering states for Albian Heavy Synthetic and for Wabiska Heavy bitumen (Hollebone 2011a&b). The results for densities are presented in Table 1, along with associated values of β calculated from eq 5 re-arranged as:

$$\beta = \frac{1}{\Delta T}\ln(\rho_b / \rho') \qquad \text{eq 5a}$$

The temperatures used for the density determinations were 0 °C and 15 °C, and the weathering states included un-weathered bitumen and bitumen samples evaporatively weathered to mass losses of 22.58% for the Albian Heavy Synthetic and to 10.65% for the Wabiska Heavy. Although the density of the un-weathered Albian Heavy Synthetic remained well below values that could sink in fresh water, comparison with eq 2 shows that the density of the un-weathered Wabiska Heavy would sink in brackish seawater at salinities as high as 13.6 ‰ at 0 °C. Weathering consistently increased bitumen density, and the weathered Albian Heavy Synthetic would sink even in nearly full-strength seawater at 0 °C. These results reflect the behaviour of these bitumen products un-diluted with solvents to reduce density and viscosity. The densities measured after the evaporative weathering therefore represent an upper bound on densities likely to be attained following release into the environment, reflecting complete loss of any solvents that might be added to facilitate pipeline transport as well as the indicated losses of bitumen components. However unlikely in actual practice, such bounds are useful for constraining the range of possibilities. In any case, the results of these tests are clearly useful for calculating coefficients of thermal expansion for bitumen products.

The coefficients of thermal expansion (β) calculated for the fresh and weathered bitumen samples evaluated by Environment Canada are also presented in Table 1. Three of the four results for β are fairly consistent, ranging from 0.000588 - 0.000642 °C^{-1}, and are comparable with values presented for crude oils in the literature (Jessup 1930, Hall et al. 1975, Hooker & Bringham 1978). However, the result for un-weathered Wabiska Heavy is larger by a factor of about six. This is far larger than any literature values, so the underlying measurements for this sample must be considered doubtful, and I will exclude this one result for β from consideration hereafter.

A second study (Belore 2010) evaluated density changes of diluted MacKay River Heavy and diluted Cold Lake bitumen at two temperatures and at three weathering states, one of which was un-weathered. A 2 cm thick layer of the diluted bitumen was placed in a wind tunnel operating at a wind speed of 3 m/s and temperature of 20 °C, and samples were collected initially and after 2 and 14 days. The density of each sample was measured at 1 °C and 15 °C. Selected results of these tests are presented here in Table 2. Despite evaporative weathering losses of 13% - 18%, the densities of all the bitumen samples remained well below the density of fresh water at corresponding temperatures (cf. eq 2), so none of them weathered sufficiently to sink under the conditions of the test. This is in part a consequence of the relatively low ratio of surface area to volume of the bitumen (0.5 cm^{-1}) that limited extent of weathering under the conditions of the tests. The surface area of a more realistic 1 mm thick slick has a ratio of surface area to volume of 0.05 cm^{-1}, and so would be expected to weather about 10 times faster.

Coefficients of thermal expansion calculated from the density measurements of MacKay River Heavy and Cold Lake diluted bitumen using eq 5a range from 0.000369 - 0000910 $°C^{-1}$ (Table 2), similar to most of the values calculated from the Environment Canada results (Table 1).

The rather artificial test conditions of the Belore (2010) study were followed by another study that attempted to simulate more realistic environmental conditions, presented by anonymous authors at SL Ross Environmental Research Ltd in October 2012 (SL Ross 2012). This study involved two tests, one with oil exposed to ambient laboratory light, and the other to laboratory light augmented with an ultraviolet (UV) lamp. In each test, 5 L of diluted Cold Lake Bitumen (CLB) were added to an oval flume channel containing fresh water, with a surface area of 4.37 m^2, implying a slick thickness of 1.15 mm. The diluted bitumen circulated in the flume channel under the influence of a 1.5 m/s (3 kt) air current and a 0.5 m/s water current, and passed beneath a cascade of water as it circulated around the flume channel to simulate turbulence. During the test with the UV lamp, the lamp illuminated one section of the flume at an intensity of 150 W/m^2. The water temperature was held at 15 ± 1 °C, and the tests were run for 5 days without UV and for 13 days with it. Samples of weathered bitumen product were removed at intervals and tested for density, viscosity and water content. Because of technical difficulties in measuring high-viscosity weathered bitumen densities at 15 °C, the density determinations were made at 20 °C.

Results of the test without the UV lamp showed that the diluted CLB rapidly incorporated water to form a meta-stable emulsion. The proportion of water increased from nil to 30% within 1.5 h, continued increasing to a maximum of 39% by 24 h, and then declined to 20% by 96.5 h (see col. 2 Table 3). The density of the bitumen-water emulsion increased from 945 kg/m^3 initially to 995 kg/m^3 after four days (col 3 Table 3). The density of the bitumen itself (ρ_b) may be calculated from these results and the density of fresh water (ρ_{fw}) at 20 °C (998.2 kg/m^3, eq 1) by equating the proportional contributions of the bitumen and the water to the observed density (ρ_{obs}):

$$\rho_b(1 - f_{fw}) + \rho_{fw}f_{fw} = (\rho_{obs}) \qquad \text{eq 6}$$

where f_{fw} is the proportion of the total mass that is fresh water. Solving eq 6 for ρ_b at 96.5 h where $f_{fw} = 0.20$ gives 994 kg/m^3 (col 4 Table 3). However, note that these densities are not the densities of the test temperature, but are densities at 20 °C, or 5 °C higher than the actual test conditions.

Results of the test with the UV lamp on resulted in faster weathering and less water incorporation compared with tests without the UV lamp (Table 3). After correcting for water incorporation using eq 6, the CLB density increased from 945 kg/m^3 initially to 998 kg/m^3 at 96 h (col. 4 Table 3), when the proportion of fresh water was 20%, the same proportion as the test without the UV lamp at 96.5 h. Inspection of the CLB density results from 96 h onwards suggests that the precision of the density measurements is not better than 1 - 2 kg/m^3. The duplicate results at 120 h, 140 h, 285 h and 311 h differ by up to 2 kg/m^3, and the range of results from 96 h onwards is 4 kg/m^3. It is unlikely that the density of the weathering CLB ever actually declines with time in these tests, because the diluted bitumen components most susceptible to loss by evaporation or dissolution are the lower molecular weight compounds that have lower densities than that of the bulk bitumen. The density measurements from 96 h onwards may therefore be taken as repetitive observations of the same asymptotic density under the conditions of the test, and their average, 997 ± 0.8 kg/m^3 (95% confidence interval, $df = 8$) will be used to calculate the coefficient of thermal expansion from this test.

Calculation of the coefficient of thermal expansion requires density determinations at two or more different temperatures, but the data presented in the SL Ross (2012) give densities only for 20 °C. However, the corresponding density at 15 °C may be inferred from the authors' observation that the weathered bitumen was very close to neutrally buoyant toward the end of the test involving the UV lamp. This implies that the weathered bitumen density was nearly identical with the density of fresh water at 15 °C (i.e. 999.10 kg/m^3). Substituting this value and the average measured density at 20 °C (997 kg/m^3) into eq 5a gives a value of $\beta = 0.000463\ °C^{-1}$, somewhat smaller than the results calculated on the basis of the earlier report for Cold Lake bitumen (Belore 2010), where β ranged from 0.000652 - 0.000910 (Table 2). The results of using this value for β to correct the density measurements at 20 °C to 15 °C conditions of the tests, with and without the UV lamp, are presented in column 5 of Table 3. In addition, this value of β can be used to determine the densities of CLB at even cooler temperatures, as will be explained in the next section.

Aqueous Temperature and Salinity Conditions Conducive to Sinking for Alberta Tar Sands Bitumen Products

The temperature and salinity conditions under which Albian Heavy Synthetic and Wabiska Heavy bitumen will sink may be determined by comparing the measured densities and coefficients of thermal expansion calculated from them in Table 1 with the results of eq 2 for specified values of temperature and salinity of the receiving water. These comparisons are presented in Figure 1, where density contours for water within a temperature range of 0 - 15 °C and a salinity range of 0 - 30 ‰ are presented along with density contours of the weathered bitumen samples from the two sources. Note that the weathered Wabiska Heavy bitumen would sink in 10 ‰ sea water at 15 °C, and would sink in nearly 20 ‰ sea water at 0 °C. The weathered Albian Heavy Synthetic bitumen would sink at salinities up to about 24 ‰ at 15 °C, and in almost full-strength seawater at 0 °C. However, without the details of the weathering procedure used at Environment Canada to produce the density measurements, it is not clear how likely spilled bitumen products would weather to the densities measured under natural ambient conditions.

A similar comparison of the temperature and salinity conditions under which weathered CLB will sink may be determined using the data presented in Table 3 for the measured densities and calculation of the coefficient of thermal expansion (i.e. $\beta = 0.000463\ °C^{-1}$). The results of this comparison are presented in Figure 2, and show that without the UV lamp, weathered CLB would begin to sink in fresh water at temperatures below about 7.7 °C, and would sink in brackish seawater at salinities as high as 4 ‰ at 0 °C, assuming that Cold Lake bitumen could weather to the density attained by exposure to the experimental treatment at 15 °C under some realistic combination of natural conditions.

The presence of the UV lamp accelerated weathering of CLB during the SL Ross (2012) experimental exposure, at least in part because of the heating effect of the lamp. The dark color of the bitumen on the circulating water surface in the exposure tank flume ensures relatively efficient absorption of the radiant energy produced by the lamp, raising the effective temperature of the surface layer of the bitumen. Most of the top of the tank was covered, which may have allowed the UV lamp to heat the air between the bitumen and tank cover, also contributing to additional heating. In any case, the extent of weathering by 96 h was sufficient to increase the density of the bitumen to near neutral buoyancy, and as shown in Figures 1 & 2, the density of bitumen products increases much faster than the water at lower temperatures. The result is first that, had these tests been conducted at 12 °C instead of 15 °C, the weathered CLB would have sunk by 96 h, and second that the weathered CLB would sink in brackish seawater at about 7.5 ‰ at 0 °C, again assuming it weathered to an equivalent extent.

To evaluate whether diluted Cold Lake bitumen could weather as rapidly at cooler temperatures and faster wind speeds as at 15 °C and 1.5 m/s, Belore (2010) provides a convenient means of evaluating the combined effects of differing combinations of temperature, wind speed, slick thickness and exposure time. Following MacKay et al. (1983), the fractional volume lost is given by:

$$F_v = \frac{\ln\left[1 + \frac{12,191}{T}\theta \exp\left(8.2 - \frac{5,239}{T}\right)\right]}{\frac{12,191}{T}} \qquad \text{eq 7}$$

where T is the ambient absolute temperature in degrees Kelvin (°K), and θ is the evaporative exposure, given by:

$$\theta = \frac{Kt}{x_0} = \frac{0.0015\ U^{0.78}\ t}{x_0} \qquad \text{eq 8}$$

where K is the mass transfer coefficient in meters per second, U is the wind speed in meters per second, t is the exposure time in seconds, and x_0 is the slick thickness in meters. For a slick thickness of 0.00115 meters, wind speed of 1.5 m/s and a temperature of 15 °C = 288 °K, which are the conditions used in the tests with Cold Lake bitumen as reported in SL Ross (2012), the fractional volume lost at 96 h from eq 7 is $F_v = 0.168$. If the wind speed increased to 4.5 m/s, according to eq 7 the same fractional volume would be lost at 5 °C. These results indicate that the bitumen densities at 96 h exposure achieved through weathering losses at 15 °C and 1.5 m/s wind speed could also be achieved at lower temperatures combined with higher wind speeds.

The above results show that for combinations of ambient temperature and wind speed that are not uncommon in the closed channel assessment area of the coast of British Columbia, evaporative weathering could plausibly lead to density increases that would result in weathered bitumen products sinking in fresh water or brackish seawater. In the next section I consider the extent and likelihood of encountering such conditions in this area.

Effects of Salinity, Temperature and Winds in the Confined Channel Assessment Area on Bitumen Density

Climatological, hydrological and oceanographic observations and records for the closed channel assessment area have been summarized by Fissel et al. (2010). These records include wind speed, seawater temperature and salinity data at several locations. These data may be used in conjunction with eqs 7 & 8 to estimate the time required for diluted CLB to weather to the same extent as occurred during the experimental tests reported by SL Ross (2012). Note that after 96 h exposure to an air current of 1.5 m/s at a temperature of 15 °C without illumination supplied by the UV lamp, diluted CLB attained a density of 996 kg/m^3, and the fractional volume lost (F_v) under these conditions is 0.168 using eq 6.

I computed "equivalent weathering times" by substituting measurements of the environmental wind speeds and surface (1.5 m depth) seawater temperatures along Kitimat Arm, Douglas Channel and Wright Sound as reported by Fissel et al. (2010) in their tables A-2, A-3 and C-5 into eq 6, and then adjusting time in that equation to find the time required to reach $F_v = 0.168$. The wind speeds were taken from measurements at the Nanakwa Shoal station in Douglas Channel. The results of these calculations are presented in Table 4 for two sets of conditions: average wind speeds, temperatures and salinities during the months of March, May, July, October and December; and maximum 1-h sustained wind speeds, minimum temperatures and minimum salinities during those same months.

The results of my calculated equivalent weathering times under average conditions show that the test conditions used for the SL Ross (2010) experimental weathering of diluted Cold Lake bitumen correspond with weathering rates that would be found during the month of March, when the average wind speed was 4.5 m/s and the sea surface temperatures were 4 - 5 °C (Table 4A). Equivalent weathering times were shorter for all the other months and locations, with July weathering times being about half those of the experiment (~48 h). While none of these combinations of average salinity and temperature would result in sinking CLB within the equivalent weathering times indicated, further weathering might well cause the bitumen to attain a density sufficient to sink. For example, if diluted bitumen achieved the same weathering state after an additional 48 h during average July wind and temperature conditions in Kitimat Arm as did the diluted Cold Lake bitumen under the SL Ross (2010) test conditions with the UV lamp on, then it would sink in the brackish salinity present (5.2 ‰).

Environmental conditions more conducive to sinking of diluted Cold Lake bitumen include maximum sustained wind speeds combined with low temperatures and salinities. In Kitimat Arm, the maximum sustained wind speed of 12 m/s during July combined with the minimum temperature of 11.8 °C and salinity of 0.3 ‰ would cause diluted CLB to sink outright within an equivalent weathering time of 25 h. Comparable calculations indicate that diluted CLB would also sink under especially conducive conditions from May through October in Kitimat arm within 31 h or less, and would probably sink after 48 h weathering in March under such conditions. Note that the equivalent weathering times calculated for these more conducive sinking conditions are usually less than 36 h, so prolonged exposure to these conditions might lead to sinking throughout the Kitimat Arm-Douglas Channel-Wright Sound waterway network.

Whether other diluted bitumen products from the Alberta tar sands are as likely as diluted Cold Lake bitumen to sink in the confined channel assessment area depends strongly on the density of the bitumen before dilution, and the volatility of the diluent. For example, if Albian Heavy Synthetic bitumen, having the properties measured by Environment Canada (Hollebone 2011a), were to be diluted with a volatile gas condensate, rapid evaporative loss of the condensate following a spill might well lead to weathered bitumen that would sink throughout most of the confined channel assessment area. To evaluate this quantitatively, much more extensive and careful testing would be needed that encompassed the range of un-diluted bitumen densities and diluent solvents that might be encountered and their likely mixing ratios, and that also considered the thermal expansion characteristics that alter the density of diluted bitumen products with temperature throughout the range of plausible weathering states.

Once spilled, diluted bitumen products will rapidly spread on the surface of receiving waters to form thin (< 1mm) slicks that would be initially buoyant but lose volatile components rapidly. Under quiescent weather conditions, slick expansion will continue to limits imposed by the surface tension of the spilled product, or until some physical barrier such as a shoreline or a density front is encountered. Density fronts are commonly encountered oceanographic features in coastal inlets, especially those receiving freshwater discharges from rivers. The lower density of the discharged fresh water tends to float above the more saline (and hence more dense) marine waters, establishing density gradients both vertically and horizontally where the fresher water meets the more saline marine waters at the sea surface. This horizontal density gradient at the sea surface may present an apparent barrier to further spreading of oil slicks. These horizontal gradients act as convergence zones where the collision of two water masses meet, and buoyant objects floating on the water surface, such as oil slicks, other organics or marine debris, tend to accumulate there. These fronts are ephemeral features, and may serve to facilitate transport of near-neutrally buoyant material to depths beneath the surface of the sea.

When two water masses of differing densities collide, the more dense water will sink beneath the less dense water. If nearly neutrally-buoyant material is conveyed to the convergence zone created by the collision, the material may be entrained into the downward motion of the sinking water mass, thus conveying the material to depth. Thus, while an oil slick may appear to be constrained from spreading by a horizontal density front, in some circumstances it may also be sinking.

In any case, such horizontal density fronts are dynamic and usually short-lived. These fronts are often dispersed by tidal mixing and by surface winds, both of which can weaken the density gradient by mixing the two water masses involved. Given the large range of tidal excursion in the region (to 6.5 m), tidal mixing can either promote or degrade surface density gradients on time scales of hours. As wind speeds increase, they will also impart a horizontal force on an oil slick, causing it to move in the direction of the wind. If strong enough, this force may readily overcome the constraints imposed by horizontal density gradients, allowing an oil slick to move across it into higher-density, more saline waters. For example, average wind speeds of 4.5 m/s will induce slick movement at about 3% of the wind speed (Reed 1989), or about 14 cm/s (0.5 km/h). Unless sustained by water currents of comparable magnitude, surface density gradients would present little impediment to wind-induced slick movement. At higher wind speeds, slick movement would be augmented by wave action through Stoke's drift (Boufadel et al. 2006). Under this mechanism buoyant oil droplets temporarily entrained into the water column under the influence of waves are transported in the direction of the waves, and this transport is also largely unimpeded by surface salinity-driven density fronts.

As shown in Table 4, diluted bitumen products from the Alberta tar sands could readily weather to densities that would sink to depths of at least 1.5 m in fresh or brackish marine receiving waters under ambient conditions encountered in the confined channel assessment area. The maximum depth of sinking depends in part on the depth of the mixed layer, which depends in turn on a number of factors such as river discharge rate, the amount of recent precipitation, and strength and duration of recent winds. Considering only density variation in the water column attributable to changes in temperature and salinity, diluted bitumen that evaporatively weathered enough to sink at the surface would disperse throughout the mixed layer, which may be only a few meters in depth. But once weathered bitumen sinks beneath the sea surface, even to a depth of only 1.5 m, other factors come into play that may facilitate sinking.

In particular, water bodies receiving river discharges of glacially-derived material will contain a load of inorganic suspended particulate material, and adhesion of any of this material scavenged from the water column onto the surface of submerged oil may increase the combined density enough to sink beneath the vertical density gradient separating the upper mixed layer from the more dense water masses below. Loading of glacially-derived suspended particulate material can be substantial (~10 mg/L) in Kitimat Arm (estimated from data presented in MacDonald 1983).

Other mechanisms that would reduce the buoyancy of weathered bitumen products once initially submerged include association with biogenic inorganic material in the water column (e.g. diatoms and zooplankton shells), and contact with fine-grained sediments on the seafloor in areas where the mixed layer extends to the bottom of the water column.

Conclusions

1. Evaluation of the susceptibility of diluted bitumen products from the Alberta tar sands must carefully consider the differing rates of thermal expansion of bitumen and receiving waters. Failure to acknowledge and carefully consider these differences can and has led to misleading conclusions regarding the likelihood that these bitumen products might sink in receiving fresh and marine waters.

2. Evaluation of the environmental risks associated with sinking bitumen products is hampered by the limited number of studies on the kinds of diluted bitumen products likely to be shipped through the proposed Northern Gateway pipeline. Testing should be done on a much wider range of candidate products, at realistic oil slick thicknesses, and at realistic environmental conditions of wind speeds, temperatures and salinities.

3. Based on the results of the limited testing available, it is clear that accidental spills of diluted bitumen products from the Alberta tar sands would often eventually sink in fresh water solely on account of evaporative weathering, and would also sink in brackish marine waters under plausible circumstances.

References

Belore, R. 2010. Properties and fate of hydrocarbons associated with hypothetical spills at the marine terminal and in the confined channel assessment area. Technical Data Report. SL Ross, Calgary, Alberta

Boufadel, M.C., Bechdel, R.D. and J. Weaver. 2006. The movement of oil under non-breaking waves. Mar. Pollut. Bull. 52:1056-1065

Fissel, D.B., Borg, K., Lemmon, D.D. and J.R. Birch. 2010. Marine physical environment. Technical Data Report, Enbridge Northern Gateway Project. ASL Environmental Sciences, Sidney, British Columbia

Hall, A.H., Simpson, J.A. and J.R. Whetstone. 1975. SP 7 Investigation of densities and thermal expansion coefficients applicable to petroleum measurement. 9th World Petroleum Conference, May 11 - 16, 1975, Tokyo, Japan

Hooker, P.R. and W.E. Brigham. 1978. Temperature and heat transfer along buried liquids pipelines. J. Pet. Tech. 30:747-749

Hollebone, B. 2011a. AHS_datasheet 2011.pdf. Personal communication via email to J. Short.

Hollebone, B. 2011b. Wabiska_datasheet 2011.pdf. Personal communication via email to J. Short.

Jessup, R.S. 1930. Compressibility and thermal expansion of petroleum oils in the range 0° to 300° C. Bureau of Standards J. Res. 5:985-1030

MacDonald, R.W. 1983. The distribution and dynamics of suspended particles in the Kitimat Fjord system. Pages 116-137 *in* Proceedings of a Workshop on the Kitimat marine environment. Canadian Technical Report on Hydrography and Ocean Sciences No. 18. Institute of Ocean Sciences, Dep't of Fisheries and Oceans, Sydney, B.C. V8L 4B2

Mackay, D., W. Stiver and P.A. Tebeau. 1983. Testing of crude oils and petroleum products for environmental purposes. In *Proceedings of the 1983 Oil Spill Conference*. American Petroleum Institute. Washington, DC. 331-337.

Millero, F.J. and A. Poisson. 1981. International one standard atmosphere equation of state for seawater. Deep Sea Res. 28A:625-629

National Energy Board. 2000. Canada's oil sands: A supply and market outlook to 2015 - an energy market assessment. National Energy Board, publications offices, 444 Seventh Avenue SW, Calgary, Alberta T2P OX8

Reed, M. 1989. The physical fates component of Natural Resource Damage Assessment model system. Oil Chem. Pollut. 5:99-123

SL Ross. 2012. Meso-scale weathering of Cold Lake bitumen/condensate blend. SL Ross Environmental Research Ltd, #200 - 1140 Morrison Drive, Ottawa, ON K2H 8S9

UNESCO. 1981. Background papers and supporting data on the International Equation of Stat of Seawater 1980. UNESCO technical papers in marine science 38. UNESCO, Paris.

Tables

Table 1. Density measurements performed by Environment Canada on Albian Heavy Synthetic and Wabisca Heavy bitumen (Hollebone, pers. comm. 2011a&b). Test conditions include 0 °C and 15 °C, and fresh and evaporatively weathered bitumen, with the percent by weight mass loss of the weathering given in the subheading for each bitumen source. The coefficients of thermal expansion are calculated from the density results using eq 5a.

		Albian Heavy Synthetic		**Wabisca Heavy**	
Weathering		**0**	**22.58%**	**0**	**10.65%**
Density (kg/m^3)	**0 °C**	946.3	1,027.1	1,010.9	1,015.8
	15 °C	937.2	1,017.4	957.2	1,006.9
β **(°C^{-1})**		0.000642	0.000634	0.003645	0.000588

Table 2. Density measurements performed by S L Ross & Co on MacKay River Heavy and Cold Lake bitumen (Belore 2010). Test conditions include 1 °C and 15 °C, and fresh and evaporatively weathered bitumen, with the percent by weight mass loss of the weathering given in the subheading for each bitumen source. The coefficients of thermal expansion are calculated from the density results using eq 5a.

		MacKay River Heavy Bitumen			**Cold Lake Bitumen**		
Weathering		**0**	**8.85%**	**12.87%**	**0**	**14.28%**	**16.99%**
Density (kg/m^3)	**1 °C**	952	970	977	948	987	990
	15 °C	943	965	970	936	977	981
β **(°C^{-1})**		0.000678	0.000369	0.000514	0.000910	0.000727	0.000652

Table 3. Experimental measurements of the effect of weathering on the density, viscosity and proportion of water incorporation for diluted Cold Lake bitumen exposed to an air current of 1.5 m/s and a slick of 1.15 mm thickness floating on

freshwater at a temperature of 15 °C. Bitumen densities are for bitumen/water emulsion (column 1), bitumen corrected for water content at 20 °C using eq 6 (column 4) and at 15 °C using results of column 4 and eq 5 (column 5; see text). Data are from SL Ross (2012).

Treatment: UV Lamp Off					
	(1)	**(2)**	**(3)**	**(4)**	**(5)**
Exposure Time (h)	**Observed Density (kg/m^3)**	**Proportion of water (f_{fw})**	**Bitumen Viscosity (cP)**	**Bitumen Density (kg/m^3)**	
				20 °C	**15 °C**
0	945	0	3,300	945	947
1.5	981	0.30	20,000	973	976
6	986	0.34	70,030	979	982
24	992	0.39	116,000	988	990
49	993	0.39	168,000	989	992
72	994	0.30	190,500	992	994
96.5	995	0.20	200,000	994	996
120.5	995	0.26	206,500	993	996
	UV Lamp On				
0	945	0	3370	945	947
0.5	968	0.26	4370	957	960
1	976	0.29	15,480	967	969
3	985	0.30	38,300	979	982
16.3	994	0.23	145,000	993	995
24	995	0.34	193,000	993	996
48	994	0.26	244,500	993	995
96	998	0.20	400,000	998	1000
120	996	0.17	420,000	996	998
120	995	0.15	442,000	994	997
140	997	0.12	382,000	997	999
140	996	0.15	550,000	996	998
285	998	0.18	825,000	998	1000
285	997	0.13	665,000	997	999
311	998	0.12	1,730,000	998	1000
311	998	0.17	1,090,000	998	1000
			Average, 96 - 311 h:	996.79	999.08
			Standard Deviation:	1.32	1.32

Table 4. Wind speeds, salinities and temperatures in Kitimat Arm, Douglas Channel and Wright Sound by selected months. A: mean wind speeds and average salinities and temperatures; B: maximum 1-h sustained wind speeds and minimum salinities

and temperatures. Salinities and temperatures at 1.5 m depths. Equivalent weathering times are the times required for diluted Cold Lake bitumen to reach the density attained under laboratory conditions after 96 h exposure to 1.5 m/s air current and 15°C as reported in Table 3 above for the "UV lamp off" treatment. Equivalent weathering times that would result in bitumen becoming more dense than the ambient seawater at the temperatures and salinities shown are in boldface. Data from Tables A-2, A-3 and C-5 of Fissel et al. 2010.

A.						
		Mar	**May**	**Jul**	**Oct**	**Dec**
Mean Wind Speed (m/s)		4.5	3.9	4.4	4.1	5.5
Average Salinity and Temperature Conditions						
Kitimat Arm	S (‰)	16.6	15.8	5.2	14.9	25.5
	T (°C)	4.2	10.1	14.3	9.0	5.2
	Equivalent Weathering Time (h)	105	67	44	71	82
Douglas Channel	S (‰)	28.7	24.8	17.9	26.3	30.7
	T (°C)	5.0	9.2	13.2	9.9	6.8
	Equivalent Weathering Time (h)	96	73	47	68	72
Wright Sound	S (‰)	29.9	27.7	21.6	28.7	30.3
	T (°C)	5.3	8.1	11.9	9.4	6.5
	Equivalent Weathering Time (h)	96	86	54	70	72
B.						
		Mar	**May**	**Jul**	**Oct**	**Dec**
Maximum 1 h Sustained Wind Speed (m/s)		16.1	15.2	12.0	15.4	18.1
Minimum Salinity and Temperature Conditions						
Kitimat Arm	S (‰)	5.9	1.5	0.3	4.4	14.7
	T (°C)	3.5	7.8	11.8	7.1	2.3
	Equivalent Weathering Time (h)	42	**29**	**25**	**31**	42
Douglas Channel	S (‰)	28.2	24.3	15.4	25.7	30.6
	T (°C)	4.9	8.7	11.2	9.8	6.5
	Equivalent Weathering Time (h)	37	27	26	24	29
Wright Sound	S (‰)	29.8	27.7	17.3	28.7	29.9
	T (°C)	5.2	8.1	10.7	9.4	6.1
	Equivalent Weathering Time (h)	36	29	28	25	31

Figures

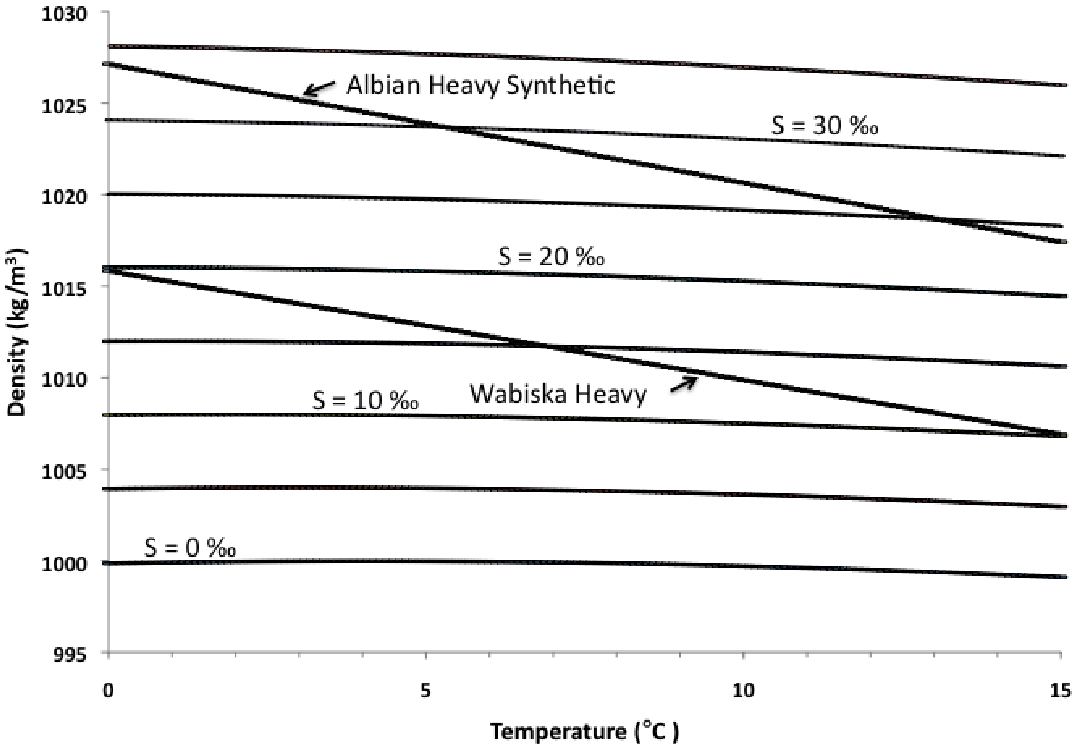

Figure 1. Comparison of densities of fresh (*S* = 0 ‰) and salt (*S* > 0 ‰) water and of weathered Albian Heavy Synthetic and weathered Wabiska Heavy bitumen samples at temperatures from 0 - 15 °C. Data based on measurements from Environment Canada (Hollebone, pers. comm. 2011a&b).

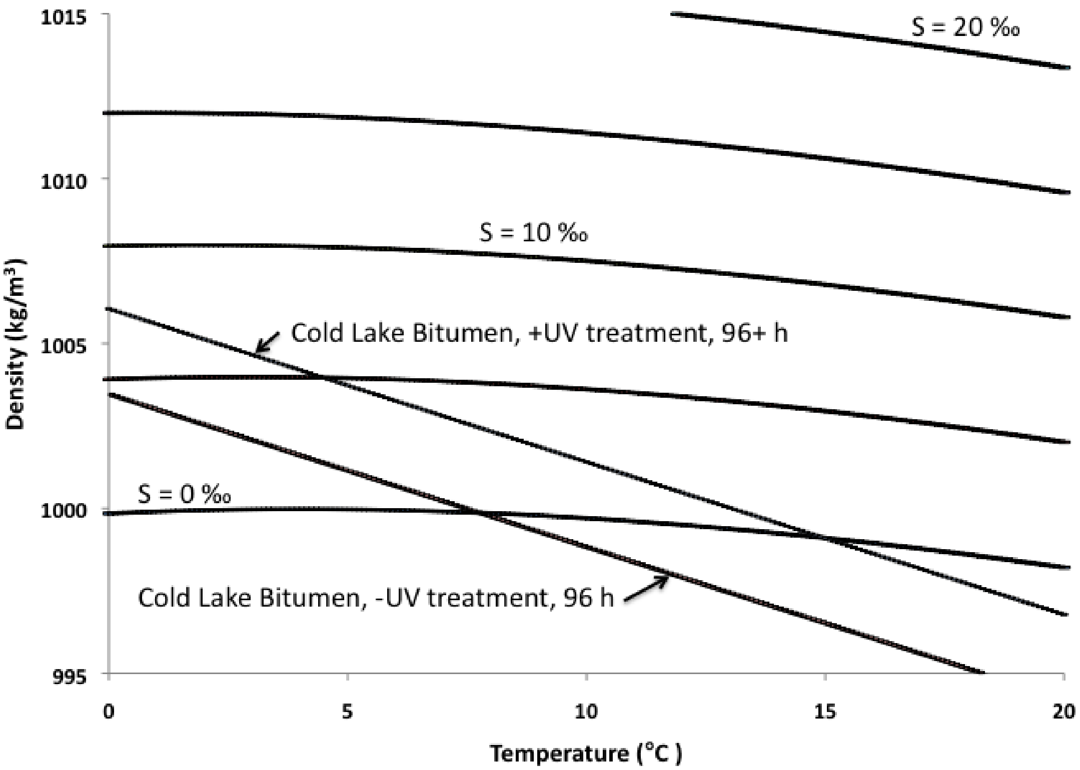

Figure 2. Comparison of densities of fresh (S = 0 ‰) and salt (S > 0 ‰) water and of experimentally-weathered Cold Lake bitumen samples in the presence and absence of a UV lamp, at temperatures from 0 - 15 °C after 96 h exposure to a 1.5 m/s air current. Data based on measurements from Belore (2010) and SL Ross (2012).

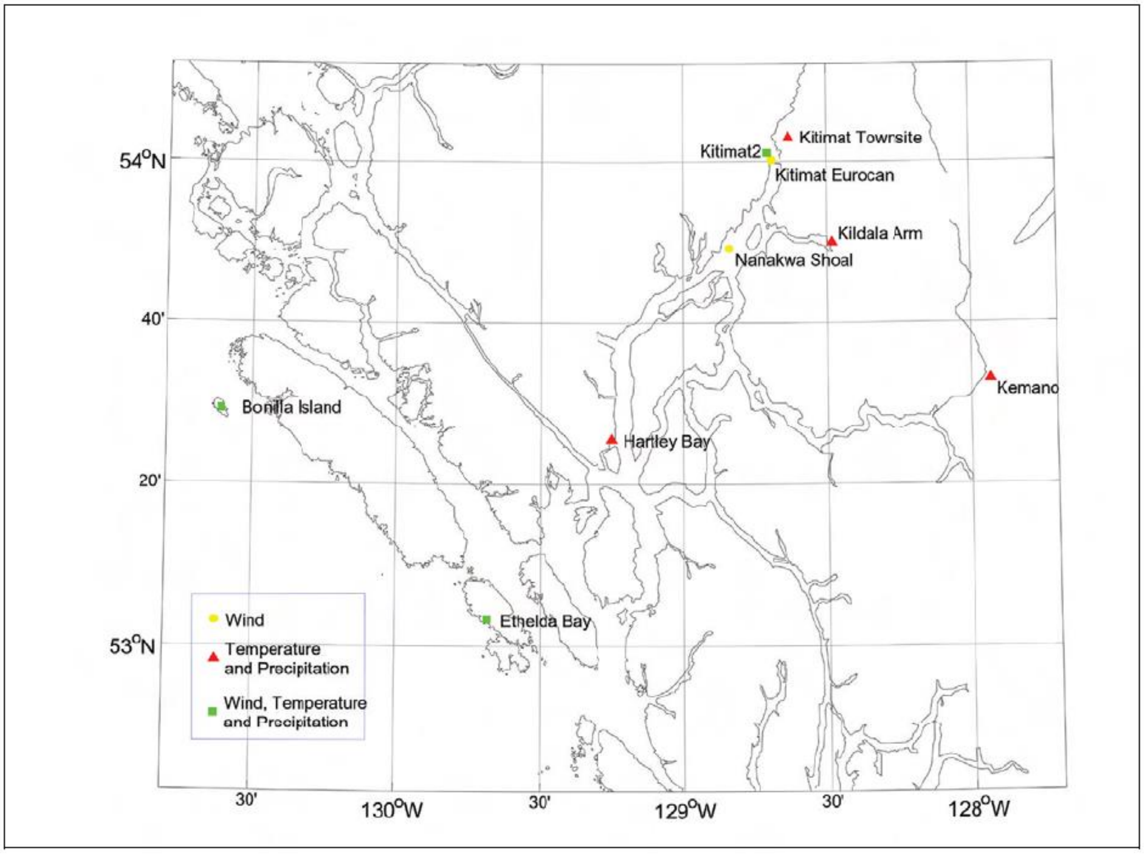

Figure 3. Location of Nanakwa Shoal, where wind speeds were measured as reported in Fissel et al. (2010, their Figure A-1).