Review of the 2015 Alaska North Slope Oil Properties Relevant to Environmental Assessment and Prediction

Prepared for

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by

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Abstract

This paper is a summary of several oil parameters and the spill behavior of the 2015 Alaskan North Slope sample as provided to Environment Canada. Environment Canada analysed the sample provided to them by PWSRCAC for environmental and physical parameters. The essential parameters included in the 2015 analysis are the oil viscosity, density, and emulsion formation.

Oil spill modeling and prediction are important facets of oil spill preparedness. The most important estimation and modeling algorithms are that for oil spill emulsification, evaporation, chemical dispersibility and those that might be used to predict other countermeasures such as mechanical recovery and burning. Oil spill modeling relies on algorithms that require a number of oil property inputs

The 2015 sample of ANS oil was found to be similar to the North Slope oils analysed in 2013 but different from those in the more distant past. It was much lighter and less viscous than those much older samples, but similar to the 2009 and 2013 samples. The environmental behavior parameters of evaporation, emulsification and dispersibility were predicted. These show that they are similar and indicative of a medium oil. The new ANS is a medium oil that does not form emulsion, is dispersible and evaporates to an extent.

Executive Summary
  The essential 2015 data are:

Table 1 Physical properties, Alaska North Slope 2015 (Hollebone, 2016)

		% Evaporative Mass Loss			
		0.00%	12.42	24.56	36.76
Density (g/mL)	0ºC	0.8751	0.9091	0.933	0.9563
	15ºC	0.8639	0.8983	0.9218	0.9444
API Gravity		31.32	25.3	21.46	17.93
Dynamic Viscosity (mPa·s)	0ºC	17.92	94.1	745.9	8427
	15ºC	9.852	36.64	170.8	1413
Surface Tension (mN/m)	0ºC	27.69	28.31	29.33	31.73
	15ºC	27.14	28.73	30.17	31.16
Interfacial Tension – Oil/Water (mN/m)	0ºC	24.09	27.57	29.89	NM
	15ºC	21.32	21.74	24.93	23.84
Interfacial Tension – Oil/Brine, 33% NaCl (mN/m)	0ºC	22.81	25.58	27.16	NM
	15ºC	19.75	22.15	28.05	23.71
Sulfur Content (%w/w)		0.9	1.1	1.3	1.4
Water Content (%w/w)		0.27%	0.01%	0.01%	0.01%
Flash Point (ºC)		NM	23.3	82.7	138
Pour Point (ºC)		-51	-48	-36	-3
Reid Vapor Pressure (K Pa) at 37.8°C		55.3	3.7	1.1	NM
Adhesion (g/m2)		18	29.3	34.3	56.4
Swirling-Flask Dispersibility (%)		45.9	51.4	51.6	4.9

Note: NM: Not Measurable due to viscosity

  The data show that this sample is similar in density to that of previous sample analyzed in 2013. The last time properties were evaluated, they were (Table 2):

Table 2 Brief History of Physical Property Values (Env. Can.)

		(all at 15°C)	
Property	**Value in 2009**	**Value in 2013**	**Value in 2015**
Density (g/mL)	0.8626	0.8649	0.8639
Viscosity (mPa.s)	13.11	14.2	9.852
Flash point (ºC)	<-5		NM
Sulfur content (%)	2.62	0.93	0.9
Saturates (%w/w)	65.28		57.8
Aromatics (%w/w)	16.51		31.9
Resins (%w/w)	14.72		6.5
Asphaltenes (%w/w)	3.49		3.8

The essential environmental facts of the 2015 sample are summarized in Table 3.

Table 3 Environmental Properties of the 2015 ANS

Evaporation	%Ev = (2.71 - 0.045T) ln t T is temperature in Celsius t is the time in minutes
Emulsification	Does not form any type Does not retain water long
Dispersibilty	~45% (Based on Swirling Flask test)

The origin and use of these predictions is illustrated in the text.

List of Acronyms and Definitions

ANS   Alaska North Slope - This usually refers to the crude oil mixture at the end of the pipeline

ASTM   American Society for Testing and Materials – a standards-setting organization

EPA   U.S. Environmental Protection Agency

FT-IR   Fourier transform-infrared

GC   Gas chromatograph - This is a chemical analytical technique.

IFT   Interfacial tension

PAH   Polycyclic aromatic hydrocarbons

PH   Phytane – an important marker found in most crude oils

PR   Pristane – an important marker, usually used in combination with Phytane to estimate biodegradation

PWSRCAC   Prince William Sound Regional Citizens' Advisory Council

Residuum   The heavy part of oil that is not distilled at normal temperatures, usually that above 535ºC

RSD   Relative standard deviation

SARA   Saturates, aromatics, resins, and asphaltenes

TMD   Trimethyl Adamantane – a marker hydrocarbon found in light oils

TMP   Trimethyl Pristane – a marker hydrocarbon found in many oils

VOCs   Volatile organic compounds

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1.   Introduction
1.1   Background
The objective of this paper is to provide properties and environmental prediction information on a 2015 sample of North Slope Alaskan crude.

1.2   Oil Properties and North Slope Crude
It is important to recognize the nature of a crude oil that stems from the inputs into the pipeline and the changing blends that occur over time. A crude oil sample drawn at one point in time from a pipeline may be completely different than a sample drawn at a later time.

The Alaska crude is an example of this principle. The Trans-Alaska Pipeline begins at Pump Station 1 (International Petroleum Encyclopedia, 2015). At this point, it is a mixture of crude oils in varying proportions from several fields. These fields include the major fields of Prudhoe Bay and Kuparuk and several minor fields including Tarn, Alpine, Fiord, Kabulkic, Milne Point, Point Mcintyre, West Beach, Point Thompson, Endicott, and Sandpiper. The characteristics of these fields vary and thus, as they are blended into Pump Station 1 at the head of the Alyeska pipeline, the starting crude varies as well. At the time of writing of this report, the Prudhoe Bay field is injecting less oil into the pipeline than prior to 2010. Some oil is withdrawn from the pipeline for the PetroStar refinery at Valdez where residual oils are re-injected into the pipeline. The sequence of this changes the composition of the oil when it is stored in Valdez.

In 2015 a new sample was drawn and the properties were measured and reported by Environment Canada. Table 1 gives these properties (Hollebone, 2016). Comparison shows that the 2015 sample is about the same as the 2013 sample in many respects (see Table 2).

1.3   A Summary of Oil Composition and Behavior
Crude oils are mixtures of hydrocarbon compounds ranging from smaller, volatile compounds to very large, non-volatile compounds (Fingas, 2015). This mixture of compounds varies according to the geological formation of the area in which the oil is found and strongly influences the properties of the oil. Petroleum products such as gasoline or diesel fuel are mixtures of fewer compounds and thus their properties are more specific and less variable. Hydrocarbon compounds are composed of hydrogen and carbon, which are therefore the main elements in oils. Oils also contain varying amounts of sulphur, nitrogen, oxygen, and sometimes mineral salts, as well as trace metals such as nickel, vanadium, and chromium.

The most common smaller and more volatile compounds found in oil are often referred to as BTEX, or benzene, toluene, ethyl-benzene, and xylenes.

Polyaromatic hydrocarbons or PAHs are compounds consisting of at least two benzene rings.

Polar compounds are those that have a significant molecular charge as a result of bonding with compounds such as sulphur, nitrogen, or oxygen. The 'polarity' or charge that the molecule carries results in behavior that is different from that of unpolarized compounds, under some circumstances. In the petroleum industry, the smallest polar compounds are called 'resins', which are largely responsible for oil adhesion. The larger polar compounds are called 'asphaltenes' because they often make up the largest percentage of the asphalt commonly used for road

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construction. Asphaltenes often have very large molecules and, if in abundance in an oil, they have a significant effect on oil behavior such as emulsification.
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1.3.1 Oil Properties

The properties of oil discussed here are viscosity, density, specific gravity, flash point, pour point, distillation fractions, and interfacial tension.

Viscosity is the resistance to flow in a liquid (Fingas, 2015). The lower the viscosity, the more readily the liquid flows. For example, water has a low viscosity and flows readily, whereas honey, with a high viscosity, flows poorly. The viscosity of the oil is largely determined by the amount of lighter and heavier fractions that it contains. The greater the percentage of light components such as saturates and the lesser the amount of asphaltenes, the lower the viscosity.

As with other physical properties, viscosity is affected by temperature, with a lower temperature giving a higher viscosity. For most oils, the viscosity varies as the logarithm of the temperature, which is a very significant variation. Oils that flow readily at high temperatures can become a slow-moving, viscous mass at low temperatures. In terms of oil spill cleanup, viscosity can affect the oil's behavior. Viscous oils do not spread rapidly, do not penetrate soil as readily, and affect the ability of pumps and skimmers to handle the oil.

The 2015 ANS oil can be compared to the old ANS oils and from Figure 1 it can be seen that the 2015 oil is about the same as the last two samples. It can be noted in Figure 1, that the sample in 2003 showed an anomalous high reading. This was probably due to chance sampling.

A comparison of viscosities appears in Table 4 below. This shows that ANS is now a typical medium crude oil in terms of viscosity.

Table 4 Typical Viscosity Comparison
 (data in mPa.s or cSt)

Comparison oils [a]	Viscosity before spilling	Viscosity after Some Weathering (mass % lost in weathering)	Viscosity after More Weathering (mass % lost in weathering)
Light crude	1	2 (30%)	5 (60%)
Medium crude	8	16 (20%)	110 (37%)
2015 ANS	10	170 (25%)	1413 (36%)
Heavy crude	820	8700 (10%)	475,000 (19%)
Dilbit	270	6300 (15%)	260,000 (30%)
Bitumen	260,000	300,000 (1%)	400,000 (2%)

[a] Light crude is represented by Scotia Light, Medium by West Texas Intermediate,
   Heavy by Sockeye Sour, and Dilbit by Cold Lake Blend

1994	21.0
1995	22.0
1996	16.0
1996	14.0
1996	18.0
2002	11.5
2004	38.9
2004	11.3
2010	13.1
2012	14.2
2015	9.9
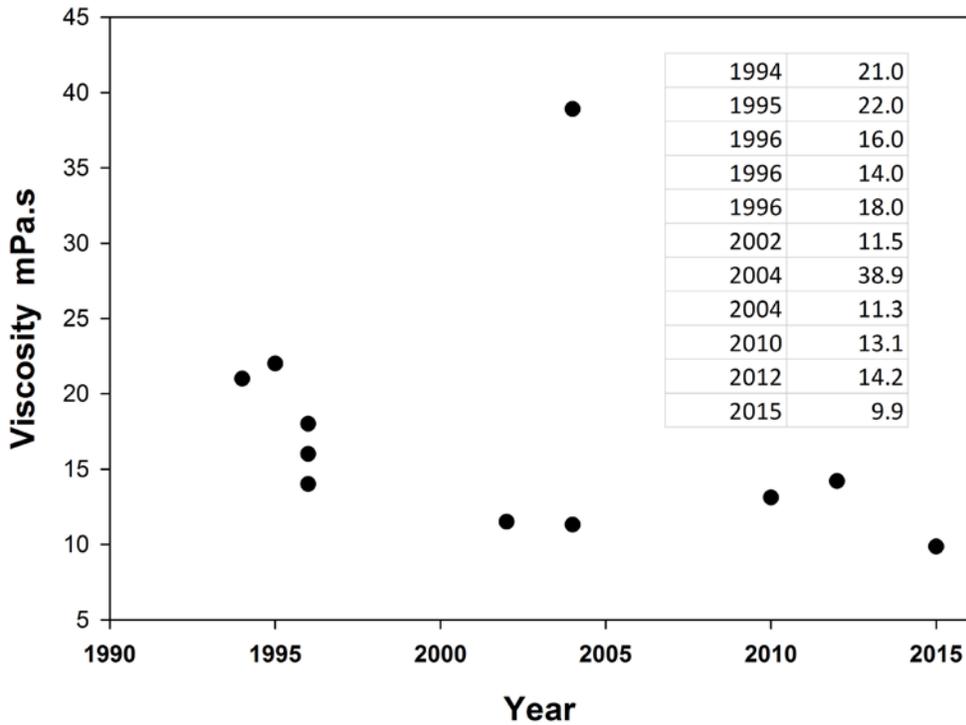
Figure 1 History of the viscosity measurements over 15 years

Density is the mass (weight) of a given volume of oil and is typically expressed in grams per cubic centimetre (g/cm^3). It is the property used by the petroleum industry to define light or heavy crude oils. Density is also important as it indicates whether a particular oil will float or sink in water. As the density of water is 1.0 g/cm^3 at 15°C and the density of most oils ranges from 0.8 to 0.99 g/cm^3, most oils will float on water. As the density of seawater is 1.03 g/cm^3, even heavier oils will usually float on it. As the light fractions evaporate with time, the density of oil increases.

Occasionally, when the density of an oil becomes greater than the density of freshwater or seawater, the oil will sink. Bulk sinking is rare, however, and happens only with a few oils, usually residual oils such as Bunker C. Significant amounts of oil have sunk, by density alone, in only about 25 incidents out of thousands.

Again to compare the 2015 sample density to the old data, one can examine Figure 2. This again shows that the 2015 sample is quite different from the very old samples, but similar to the last 2 samples. As can be seen from Figure 2, the ANS is progressing more and more to that of a lighter oil. The progression has been constant over the past 15 years.

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1994	0.8922
1995	0.8948
1996	0.8869
1996	0.8828
1996	0.8875
2002	0.8777
2004	
2004	0.8770
2010	0.8626
2012	0.8649
2015	0.8639
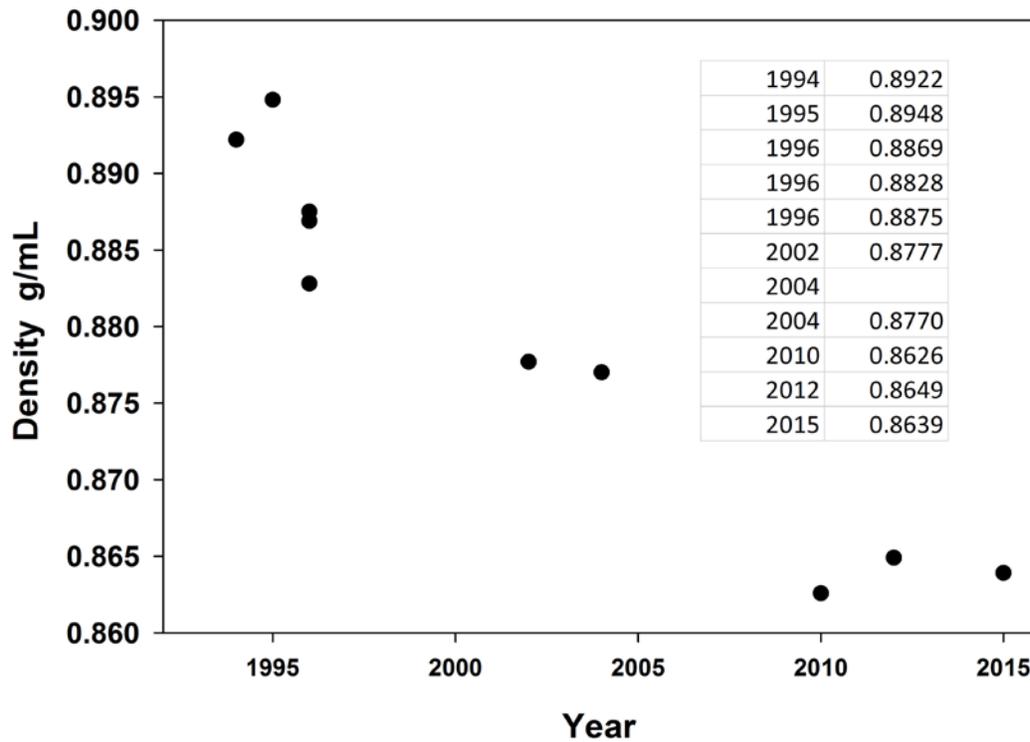
Figure 2 History of the density measurements over 15 years.

Table 5 shows the comparison of density to other oils. This shows again that the density is that of a typical medium crude oil.

Table 5 Typical Density Comparison

(data in g/mL at 15ºC, freshwater has a density of 1.00, seawater of 1.03)

Comparison oils[a]	Density before spilling	Density after Some Weathering (mass % lost in weathering)	Density after More Weathering (mass % lost in weathering)
Light crude	0.77	0.8 (30%)	0.84 (60%)
Medium crude	0.85	0.87 (16%)	0.90 (32%)
2015 ANS crude	0.86	0.92 (25%)	0.94 (37%)
Heavy crude	0.94	0.97 (10%)	0.98 (19%)
Dilbit	0.919	.983 (15%)	1.002 (30%)
Bitumen	0.998	1.002(1%)	1.004(2%)

[a] Light crude is represented by Scotia Light, Medium by West Texas Intermediate,

   Heavy by Sockeye Sour, and Dilbit by Cold Lake Blend

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Another measure of density is specific gravity, which is an oil's relative density compared to that of water at 15°C. It is the same value as density at the same temperature. Another gravity scale is that of the American Petroleum Institute (API). The API gravity is based on the density of pure water which has an arbitrarily assigned API gravity value of 10° (10 degrees). Oils with progressively lower specific gravities have higher API gravities.

The following is the formula for calculating API gravity: API gravity = [141.5 ÷ (density at 15.5°C)] - 131.5. Oils with high densities have low API gravities and vice versa. In the United States, the price of a specific oil may be based on its API gravity as well as other properties of the oil.

The flash point of an oil is the temperature at which the liquid gives off sufficient vapours to ignite upon exposure to an open flame. A liquid is considered to be flammable if its flash point is less than 60°C. There is a broad range of flash points for oils and petroleum products, many of which are considered flammable, especially when fresh. Gasoline, which is flammable under all ambient conditions, poses a serious hazard when spilled. Many fresh crude oils have an abundance of volatile components and may be flammable for as long as one day until the more volatile components have evaporated. On the other hand, Bunker C and heavy crude oils are not generally flammable when spilled. Flash point generally correlates with many of the other data such as density, distillation data, etc. The flash point of the fresh oil was not measured – probably because it was high and variable. The flash point of the weathered fractions of ANS show that it is not flammable after weathering for about ½ day. There is no historical comparison point for this value as it was not measured in the past. A comparison to other oils is shown in Table 6 below.

Table 6   Typical Flash Point Comparison

(data in °C)

Comparison oils[a]	Flash Point before spilling	Flash Point after Some Weathering (mass % lost in weathering)	Flash Point after More Weathering (mass % lost in weathering)
Light crude	<-30	35 (30%)	95 (60%)
Medium crude	-10	50 (15%)	> 110 (32%)
2015 ANS crude	not measured	83 (25%)	138 (37%)
Heavy crude	-3	67 (10%)	>95 (19%)
Dilbit	< -35	>60 (15%)	>70 (30%)
Bitumen	> 100	> 100 (1%)	>110 (2%)

[a] Light crude is represented by Scotia Light, Medium by West Texas Intermediate, Heavy by Sockeye Sour, and Dilbit by Cold Lake Blend

The pour point of an oil is the temperature at which it takes longer than a specified time to pour from a standard measuring vessel. As oils are made up of hundreds of compounds, some of which may still be liquid at the pour point, the pour point is not the temperature at which the oil will no longer pour. The pour point represents a consistent temperature at which an oil will pour very slowly and therefore has limited use as an indicator of the state of the oil. In fact, pour point has been used too much in the past to predict how oils will behave in the environment. For example, waxy oils can have very low pour points, but may continue to spread slowly at that temperature and can evaporate to a significant degree. Because pour point is not the solidification point of oil, it is not the best predictor of how oil will behave or even more specifically, how it will move in the environment. Pour point is often used incorrectly as an important parameter of oil behavior. Pour point has been measured in this sample run and this is found to be very low (less than $>0\ ^{o}$C) which indicates that the oil is quite mobile, even when weathered.

Distillation fractions of an oil represent the fraction of an oil (generally measured by volume) that is boiled off at a given temperature. This data is obtained on most crude oils so that oil companies can adjust parameters in their refineries to handle the oil. This data also provides environmental scientists with useful insights into the chemical composition of oils. For example, while 70% of gasoline will boil off at 100°C, only about 5% of a crude oil will boil off at that temperature and an even smaller amount of a typical Bunker C. The distillation fractions correlate strongly to the composition of the oil as well as to other physical properties of the oil. Distillation fractions are often used to predict evaporation rates.

Figure 3 compares the change in the fraction of oil distilled at 180°C, the point used to develop evaporation equations. This again illustrates the change in ANS over the years. This shows that the recent sample appears to be lower in boiling point, however related data such as evaporation equations show that the sample is fairly consistent to previous years.
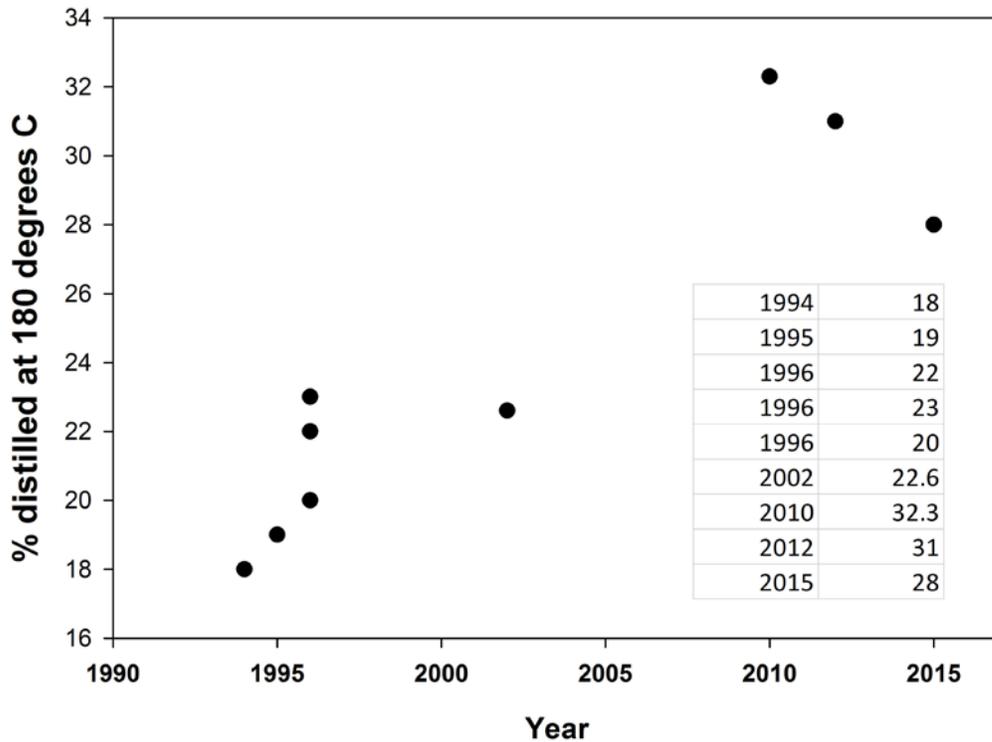
Figure 3 History of the percent distilled at 180ºC

The sulfur content of oil is sometimes included with properties, even though it is a chemical composition item. This is because sulfur content is an important consideration when considering emissions such as automotive emissions as well as considering the type of refining processes that are required for a particular type of oil. Sulfur content is also indicative of the number of polar compounds in the oil. Figure 4 shows the history of fresh ANS sulfur content over the past 15 years. This shows that the sulfur content is decreasing somewhat.

The oil/water interfacial tension, sometimes called surface tension, is the force of attraction or repulsion between the surface molecules of oil and water. Together with viscosity, surface tension is an indication of how rapidly and to what extent an oil will spread on water. The lower the interfacial tension with water, the greater the extent of spreading. In actual practice, the interfacial tension must be considered along with the viscosity because it has been found that interfacial tension alone does not account for spreading behavior. A comparison of interfacial tension shows that there has been no significant change in the past few years, and it was not measured in earlier years.
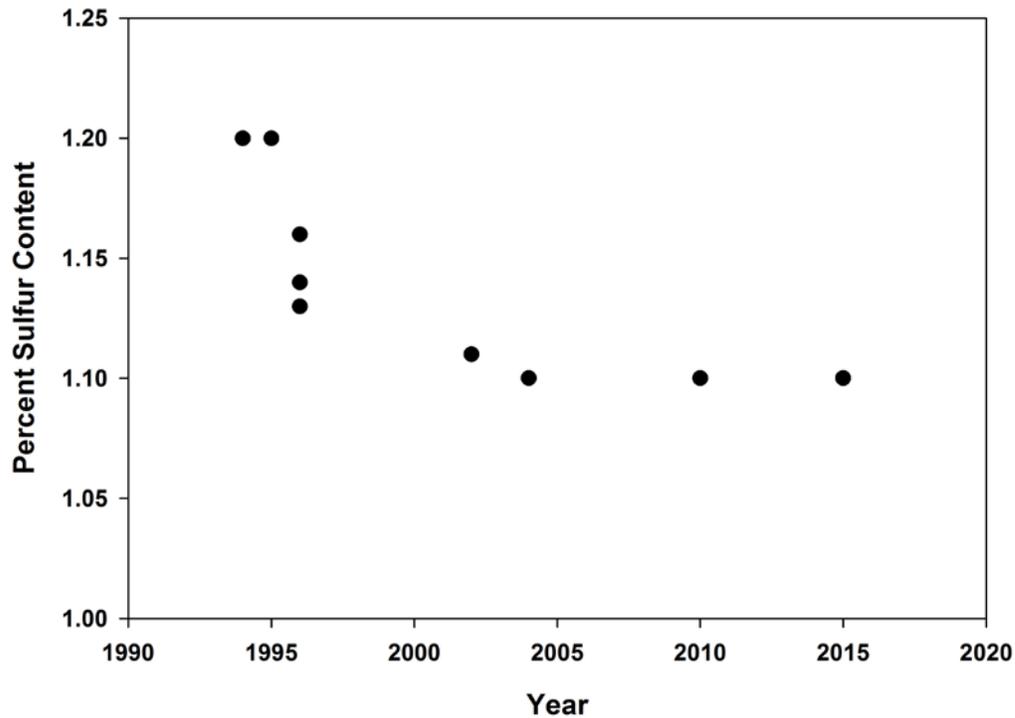
Figure 4 The history of the sulfur content of fresh ANS oil

The vapour pressure of an oil is a measure of how the oil partitions between the liquid and gas phases, or how much vapour is in the space above a given amount of liquid oil at a fixed temperature. Because oils are a mixture of many compounds, the vapour pressure changes as the oil weathers. Vapour pressure is difficult to measure and is not frequently used to assess oil spills. Vapour pressure was measured for ANS for the first time in this round, so there is no comparison point to old measurements. This may set a baseline however, if future measurements are carried out.

The ANS adhesion was measured for the first time. The adhesion test was developed to provide a standard method for measuring 'stickiness', which does vary among oils. This test can give an indication of the interaction of oil with shorelines as well as the ability to recover oil with adsorbent skimmers. High values indicate oil that may be hard to cleanup from shorelines and low values, oils that will not adhere to shorelines, but are difficult to cleanup with sorbent-surface skimmers. Table 7 shows a comparison of the adhesion of the 2015 ANS sample compared to some other oils. ANS fits right in as a medium oil and has the expected adhesion properties.

Table 7   Typical Adhesion Comparison

(data in g/m²)

Comparison oils[a]	Adhesion before spilling	Adhesion after Some Weathering (mass % lost in weathering)	Adhesion after More Weathering (mass % lost in weathering)
Light crude	0	2.5 (30%)	9 (60%)
Medium crude	12	22 (15%)	33 (32%)
ANS 2015 crude	18	34 (25%)	56 (37%)
Heavy crude	75	100 (10%)	600 (19%)
Dilbit	98	146 (6%)	1580 (20%)**
Bitumen	575		

[a] Light crude is represented by Scotia Light, Medium by West Texas Intermediate,

    Heavy by Sockeye Sour, and Dilbit by Cold Lake Blend

** highly weathered

1.3.2   Behavior of Oil

Oil spilled on water undergoes a series of changes in physical and chemical properties which in combination are termed 'weathering' (Fingas, 2015). Weathering processes occur at very different rates, but begin immediately after oil is spilled into the environment. Weathering rates are not consistent throughout the duration of an oil spill and are usually highest immediately after the spill.

Evaporation is usually the most important weathering process. It has the greatest effect on the amount of oil remaining on water or land after a spill. Over a period of several days, a light fuel such as gasoline evaporates completely at temperatures above freezing, whereas only a small percentage of a heavier Bunker C oil evaporates. The rate at which an oil evaporates depends primarily on the oil's composition. The more volatile components an oil or fuel contains, the greater the extent and rate of its evaporation. Many components of heavier oils will not evaporate at all, even over long periods of time and at high temperatures.

Oil and petroleum products evaporate in a slightly different manner than water and the process is much less dependent on wind speed and surface area than on temperature. Oil evaporation can be considerably slowed down by the formation of a 'crust' or 'skin' on top of the oil. This happens primarily on land where the oil layer does not mix with water. The skin or crust is formed when the smaller compounds in the oil are removed, leaving the larger compounds, such as waxes and resins, at the surface. These components seal off the remainder of the oil and prevent evaporation. Stranded oil from old spills has been re-examined over many years and it has been found that, when this crust has formed, there is no significant evaporation in the oil underneath. When this crust has not formed, the same oil could be weathered to the hardness of wood.

The rate of evaporation is very rapid immediately after a spill and then slows considerably. About 80% of evaporation occurs in the first few days after a spill. The evaporation of most oils follows a logarithmic curve with time. Some oils such as diesel fuel, however, evaporate as the square root of time, at least for the first few days. This means that the evaporation rate slows very rapidly in both cases. The properties of an oil can change significantly with the extent of evaporation. If about 40% (by weight) of an oil evaporates, its viscosity could increase by as much as a thousand-fold. Its density could rise by as much as 10% and its flash point by as much as 400%. The extent of evaporation can be the most important factor in determining properties of an oil at a given time after the spill and in changing the behavior of the oil.

Emulsification is the process by which one liquid is dispersed into another one in the form of small droplets. Water droplets can remain in an oil layer in a stable form and the resulting material is completely different. These water-in-oil emulsions are sometimes called 'mousse' or 'chocolate mousse' as they resemble this dessert. In fact, both the tastier version of chocolate mousse and butter are common examples of water-in-oil emulsions.

The mechanism of emulsion formation is not yet fully understood, but it probably starts with sea energy forcing the entry of small water droplets, about 10 to 25 μm (or 0.010 to 0.025 mm) in size, into the oil. If the oil is only slightly viscous, these small droplets will not leave the oil quickly. On the other hand, if the oil is too viscous, droplets will not enter the oil to any significant extent. Once in the oil, the droplets slowly gravitate to the bottom of the oil layer. Any asphaltenes and resins in the oil will interact with the water droplets to stabilize them. Depending on the quantity of asphaltenes and resins, an emulsion may be formed. The conditions required for emulsions of any stability to form may only be reached after a period of evaporation. Evaporation lowers the amount of low-molecular weight compounds in the oil and increases the viscosity to the critical value.

Water can be present in oil in four ways. First, some oils contain about 1% water as soluble water. This water does not significantly change the physical or chemical properties of the oil. The second way is called 'entrainment', whereby water droplets are simply held in the oil by its viscosity to form an unstable emulsion. These are formed when water droplets are incorporated into oil by the sea's wave action and there are not enough asphaltenes and resins in the oil or if there is a high amount of aromatics in the oil which stabilizes the asphaltenes and resins, preventing them from acting on the water droplets. Unstable emulsions break down into water and oil within minutes or a few hours, at most, once the sea energy diminishes. The properties and appearance of the unstable emulsion are almost the same as those of the starting oil, although the water droplets may be large enough to be seen with the naked eye.

Meso-stable emulsions represent the third way water can be present in oil. These are formed when the small droplets of water are stabilized to a certain extent by a combination of the viscosity of the oil and the interfacial action of asphaltenes and resins. For this to happen, the asphaltene or resin content of the oil must be at least 3% by weight. The viscosity of meso-stable emulsions is 20 to 80 times higher than that of the starting oil. These emulsions generally break down into oil and water or sometimes into water, oil, and stable emulsion within a few days. Semi- or meso-stable emulsions are viscous liquids that are reddish-brown or black in colour.

The fourth way that water exists in oil is in the form of stable emulsions. These form in a way similar to meso-stable emulsions except that the oil must contain at least 4 to 8% asphaltenes. The viscosity of stable emulsions is 800 to 1000 times higher than that of the starting oil and the emulsion will remain stable for weeks and even months after formation. Stable emulsions are reddish-brown in colour and appear to be nearly solid. Because of their high viscosity and near solidity, these emulsions do not spread and tend to remain in lumps or mats on the sea or shore.

The formation of emulsions is an important event in an oil spill. First, and most importantly, it substantially increases the actual volume of the spill. Emulsions of all types contain about 60 to 80% water and thus when emulsions are formed the volume of the oil spill more than triples. Even more significantly, the viscosity of the oil increases by as much as 1000 times, depending on the type of emulsion formed. For example, a highly viscous oil such as a motor oil can triple in volume and become almost solid through the process of emulsification.

These increases in volume and viscosity make cleanup operations more difficult. Emulsified oil is difficult or impossible to disperse, to recover with skimmers, or to burn. Emulsions can be broken down with special chemicals in order to recover the oil with skimmers or to burn it. It is thought that emulsions break down into oil and water by further weathering, oxidation, and freeze-thaw action. Meso- or semi-stable emulsions are relatively easy to break down, whereas stable emulsions may take months or years to break down naturally.

Emulsion formation also changes the fate of the oil (Fingas and Fieldhouse, 2009, 2011). It has been noted that when oil forms stable or meso-stable emulsions, evaporation slows considerably. Biodegradation also appears to slow down. The dissolution of soluble components from oil may also cease once emulsification has occurred.

2.   Summary of ANS Behavior

An important facet of understanding the oil behavior is to use actual data on the behavior of the oil. The Environment Canada report lists several important behavior data (Hollebone, 2016). These results will be reported here.

2.1   ANS Evaporation

Oil evaporation was measured by Environment Canada using pan evaporation. This resulted in an equation: $\% Ev = (2.71 - 0.045T)\ln t$ (1)

This is an empirical equation derived from controlled experiments. Figure 5 shows the predicted evaporation at different temperatures. This shows that the 2015 ANS would evaporate significantly at normal ambient temperatures within a few days.
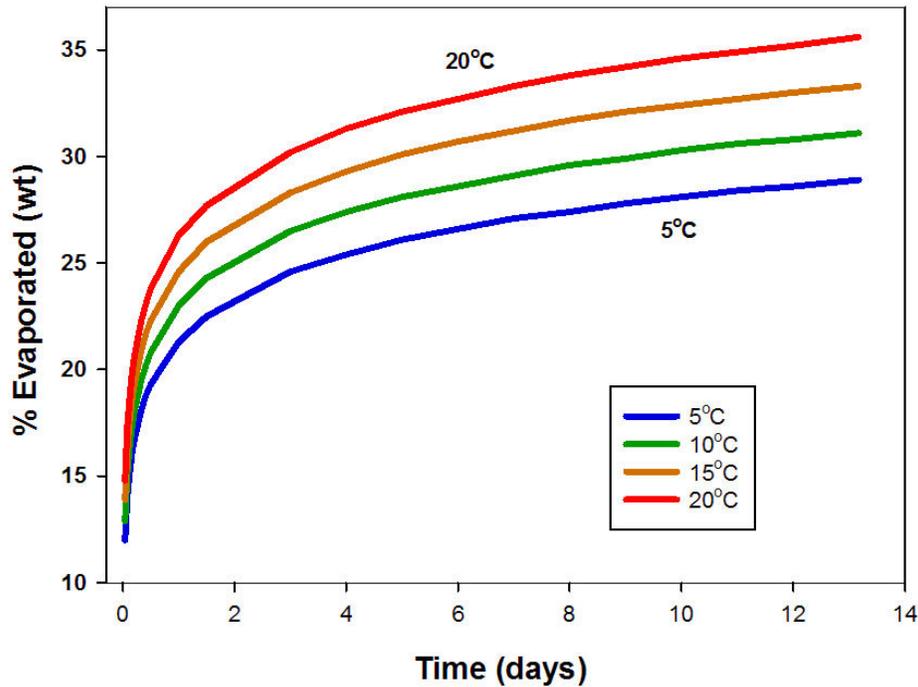
Figure 5 The evaporation of the 2015 ANS Sample

2.2   Emulsification

A test of the emulsification of this 2015 sample of ANS showed that it does not produce any form of stable emulsions. This is basically good news, as it shows that the oil would be easy to recover even after weathering. Table 8 shows the results.

Table 8   Emulsion Formation, Alaska North Slope 2015 (Hollebone, 2016)

	Fresh (0%)	W1 (12.42%)	W2 (24.56%)	W3 (36.76%)	
% Evaporative Mass Loss					
Emulsion Age (hrs)	24-hrs	24-hrs	24-hrs	24-hrs	7-day
Visual Stability Emulsion	Unstable	Unstable	Unstable	unstable-entrained*	unstable-entrained
Stress Tau (Pa)	0.4	0.4	0.6	6.1	7
Complex Modulus (Pa)	0.35	0.5	1.6	15.4	12.2
Storage Modulus (Pa)	0.2	0.1	0.1	0.9	1.1
Loss Modulus (Pa)	0.3	0.4	1.2	15.4	12.1
tan delta (V/E)	1.9	3.2	12	21.3	12.9
Complex Viscosity (Pa.s)	0.066	0.1	0.2	2.4	1.9
Water content (%w/w)	0.04	0.2	1.03	22.8	14.8

this had not been seen before and is best described as a bit of emulsion in an otherwise unstable mass

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The parameters in Table 8 are standard characterizations of heavy oils or emulsions, explanations can be found in rheological introductions (Malvern, 2016).

3.   Chemistry of ANS

Crude oils are complex mixtures of hydrocarbons and hydrocarbons combined with other elements ranging from smaller, volatile compounds to very large, nonvolatile compounds. The mixture of compounds varies with the geological formation of the area in which the crude oil is found. Crude oils are often similar in a given region and when drawn from a similar reservoir. Petroleum products such as gasoline and diesel fuel are mixtures of fewer compounds and are refined to specific standards. Thus their properties are more specific and less variable. Crude oil contains many compounds of different sizes and different classes. In fact, there are so many that as time goes by more and more compounds are identified in oil. Currently, analysts have preliminarily identified up to 17,500 compounds in an oil. In the future, this number will no doubt rise significantly.

The gas chromatographic characteristics of ANS are shown in Table 9.

Table 9 GC-Detectible Hydrocarbons, Alaska North Slope 2015 (Hollebone, 2016)

	Fresh	W1	W2	W3
% Evaporative Mass Loss	(0%)	(12.42%)	(24.56%)	(36.76%)
TPH (mg/g oil)	547	572	614	558
TSH (mg/g oil)	353	382	396	353
TAH (mg/g oil)	194	190	218	206
Resolved Peaks (mg/g oil)	135	152	146	100
TSH/TPH (%)	64.5	66.8	64.5	63.2
TAH/TPH (%)	35.5	33.2	35.5	36.8
Resolved Peaks/TPH (%)	24.9	26.6	22.2	16.1

Table 9 shows some interesting data. The TPH is the total petroleum hydrocarbons and this represents the total amount that the GC can detect out of the sample injected. For the fresh oil, Table 9 shows that this value is 547 mg (out of 1000). This amounts to 54.7 %. The remainder of the oil did not make it through the column. This is very important in considering an oil as any measurements made of it are only analyzing 54.7%. For example, if studying biodegradation, one can be fooled into thinking that the remainder is degraded, whereas it is not analyzed. Similarly, the TSH is the total saturate hydrocarbons which is the fraction of the TPH that is detected as saturate compounds. The TAH is the total aromatic hydrocarbons. This is the fraction of the oil that is detected as aromatic hydrocarbons. The 'resolved peaks' is the fraction of the oil detected in the peaks that have been resolved or separated by the GC. The remainder of the TPH is in unresolved peaks or in 'humps' in the chromatogram. The TSH/PPH and TAH/TPH ratios are indices of the saturate and aromatic components in the oil.

The saturates, aromatics, resins and asphaltene (SARA) composition of oil is a more general analytical method which defines oils by precipitation and then weight. Newer methods

now employ thin layer chromatography, the values from both methods vary somewhat. This method is still useful however, and it provides useful data both to the refiner and to the environmentalist. Saturates are hydrocarbon compounds with the maximum number of hydrogens. Aromatics are hydrocarbon compounds with at least one benzene ring. Resins and asphaltenes are larger compounds containing mostly carbon and hydrogen, but containing other elements such as oxygen, sulfur, nitrogen and metals. Table 10 shows the SARA composition of the latest fraction of ANS oil. SARA data is used extensively for fate and behavior prediction.

Table 10 Hydrocarbon Groups Analysis, Alaska North Slope 2015 (Hollebone, 2016)

% Evaporative Mass Loss	Fresh (0%)	W1 (12.42%)	W2 (24.56%)	W3 (36.76%)
%Saturates (%w/w oil)	57.8	58.9	55.6	51.5
%Saturate: Waxes (%w/w oil)	4	4.4	4.8	6
%Aromatics (%w/w oil)	31.9	29.3	30.7	30.5
%Resins (%w/w oil)	6.5	7.2	8.3	10.7
%Asphaltenes (%w/w oil)	3.8	4.6	5.4	7.7

Alkanes, an important part of saturate composition, are hydrocarbons with a chain-like structure and without double bonds or other elements such as sulphur, nitrogen or oxygen attached. Alkanes, sometimes called paraffins, are typically the most abundant compounds in crude oils as well as in most fuels such as diesel fuel and gasoline. Most crude oils have anywhere between a few percent up to 30% alkanes. Alkanes are typically the target compounds sought by petroleum producers. It should be noted, however, that larger alkanes are also called waxes, and these are sometimes less desirable from a petroleum-producers point of view. Table 11 shows the alkane compounds in the latest fraction of ANS oil. Table 11 shows that the latest sample of oil is typical of medium crude oil and contains a large proportion of refinable material. Further, the alkanes content shows the spill responder that the oil weathers to a greater extent or lesser extent. Many of the alkanes below about C20 are lost in the first few days.

Polyaromatic hydrocarbons or PAHs are compounds consisting of at least two benzene rings. PAHs make up between 0 and 60% of the composition of oil. Common PAHs and their substituted counterparts in ANS are shown in Table 12. As these are easily separated, there are extensive data on their presence in oils. These compounds have also been used somewhat as indicators of presence of certain types of oils. The concern with these compounds is that many of them are known to be relatively toxic and some to be carcinogenic. Few of the more toxic compounds are found in ANS oil. These and other PAHs are shown in Table 13.

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Table 11   n-Alkanes, Alaska North Slope 2015 (Hollebone, 2016)

% Evaporative Mass Loss	Fresh (0%)	W1 (12.42%)	W2 (24.56%)	W3 (36.76%)
	µg/g	µg/g	µg/g	µg/g
Alkanes				
n-C9	4102	3888	1222	1.2
n-C10	3656	3694	2771	0.48
n-C11	3208	3322	3235	3.01
n-C12	3057	3228	3402	308
n-C13	2850	3031	3234	1648
TMD	840	927	1009	723
n-C14	2599	2855	3069	2570
n-C15	2199	2392	2576	2574
n-C16	2024	2212	2382	2574
TMP	1037	1145	1265	1404
n-C17	2093	2265	2436	2363
Pristane	882	971	889	1106
n-C18	1686	1791	1964	2235
Phytane	974	1169	1285	1442
n-C19	1579	1675	1880	2103
n-C20	1467	1598	1730	1941
n-C21	1406	1498	1667	1901
n-C22	1343	1466	1594	1778
n-C23	1279	1399	1524	1714
n-C24	1213	1315	1386	1558
n-C25	1152	1261	1430	1583
n-C26	1082	1188	1301	1494
n-C27	876	918	1042	1197
n-C28	691	760	874	993
n-C29	576	662	722	827
n-C30	480	474	646	686
n-C31	403	454	524	623
n-C32	307	348	403	479
n-C33	262	299	348	417
n-C34	204	238	275	334
n-C35	194	227	266	327
n-C36	151	169	209	246
n-C37	116	166	190	224
n-C38	88.4	106	137	152
n-C39	60.3	71.9	88.6	104
n-C40	43.1	56.7	64.6	79.6
Total n-alkanes (µg/g)	46178	49237	49039	39709
Diagnostic indexes				
n-C17/Pristane	2.37	2.33	2.74	2.14
n-C18/Phytane	1.73	1.53	1.53	1.55
Pr/Ph	0.91	0.83	0.69	0.77
Odd alkanes	22354	23527	22384	17607
Even alkanes	18333	19570	20148	15582
CPI	1.22	1.2	1.11	1.13

Table 12   PAHs and alkyl PAHs, Alaska North Slope 2015 (Hollebone, 2016)

Alkylated PAHs		GMM g/mol	QI m/z	Fresh µg/g oil	W1 (12.42%) µg/g oil	W2 (24.56%) µg/g oil	W3 (36.76%) µg/g oil
Naphthalene	C0-N	128	128	501	497	562	18.6
	C1-N	142	142	1377	1430	1645	651
	C2-N	156	156	2071	2163	2550	2074
	C3-N	170	170	1809	1877	2253	2358
	C4-N	184	184	961	1034	1232	1361
	Sum			6719	7001	8242	6464
Phenanthrene	C0-P	178	178	177	189	223	259
	C1-P	192	192	486	513	610	698
	C2-P	206	206	510	555	651	773
	C3-P	220	220	378	419	481	591
	C4-P	234	234	176	201	235	274
	Sum			1727	1877	2200	2595
Dibenzothiophene	C0-D	184	184	107	114	136	155
	C1-D	198	198	223	242	285	325
	C2-D	212	212	314	329	400	466
	C3-D	226	226	259	297	354	416
	C4-D	240	240	178	194	220	263
	Sum			1081	1176	1395	1624
Fluorene	C0-F	166	166	66.2	69.8	83.7	88
	C1-F	180	180	152	166	189	223
	C2-F	194	194	220	242	301	334
	C3-F	208	208	234	241	289	341
	Sum			672	719	862	986
Fluoranthene/pyrene	C0-Fl	202	202	4.26	4.8	5.56	6.67
	C1-Fl	216	216	50.8	56.9	60.4	77.6
	C2-Fl	230	230	87.8	95.9	107	136
	C3-Fl	244	244	104	111	132	151
	C4-Fl	258	258	78.5	86.2	99.4	116
	Sum			325	355	405	488
Benzonaphthothiophene	C0-B	234	234	41.1	43	52.2	62.1
	C1-B	248	248	137	148	178	211
	C2-B	262	262	108	116	112	128
	C3-B	276	276	174	191	226	262
	C4-B	290	290	115	128	146	171
	Sum			575	626	714	834
Chrysene	C0-C	228	228	29.7	32.7	39.9	44.9
	C1-C	242	242	53.5	58.9	71.4	84.3
	C2-C	256	256	79	81.3	96.9	119
	C3-C	270	270	82.6	108	113	123
	C4-C	284	284	110	134	144	165
	Sum			355	415	465	536

GMM = Gram Molecular Mass
QI = Quantitation Ion

Table 13 Individual PAH and aPAH, Alaska North Slope 2015 (Hollebone, 2016)

Alkylated PAHs	Abbrev.	GMM g/mol	QI m/z	Fresh (0%) µg/g oil	W1 (12.42%) µg/g oil	W2 (24.56%) µg/g oil	W3 (36.76%) µg/g oil
Retene	R	234	234	22.2	22.6	26.8	32.5
4-Methyldibenzothiphene		198	198	109	117	137	159
2-/3-Methyldibenzothiphene		198	198	72.4	79.3	94.9	109.1
1-Methyldibenzothiphene		198	198	37.8	40.5	47.9	56.1
3-Methylphenanthrene		192	192	99	106	125	147
2-Methylphenanthrene		192	192	111	119	141	166
1-Methylanthracene		192	192	3.12	3.39	3.66	3.64
9/4-Methylphenanthrene		192	192	152	162	191	224
1-Methylphenanthrene		192	192	116	124	146	173
2-Methylnaphthalene		192	192	792	823	940	353
1-Methylnaphthalene		192	192	586	607	704	299
2,6-Dimethylnaphthalene		156	156	253	267	314	240
1,6,7-trimethylnaphthalene		170	170	136	143	171	181
Total alkylated PAHs				11454	12169	14282	13527
Other parent PAHs							
Biphenyl (Bph)	Bph	154	154	125.2	127.4	150.9	124.3
Acenaphthylene (Acl)	Acl	152	152	13.6	13.9	16.6	13.5
Acenaphthene (Ace)	Ace	154	153	14.8	13.8	18.5	13.5
Dibenzofuran	DB	168	168	47.1	48.4	57.3	47.3
Anthracene (An)	An	178	178	3.32	4.26	4.27	4.16
Fluoranthene (Fl)	Fl	202	202	5.18	5.65	6.36	5.52
Pyrene (Py)	Py	202	202	15.8	16.7	18.7	16.3
Benzo[b]fluorene(BbF)	BbF	216	216	21.2	24.1	28	34.8
Benz(a)anthracene (BaA)	BaA	228	228	2.81	2.98	4.02	2.91
Benzo(b)fluoranthene (BbF)	BbFl	252	252	4.74	5.31	6.2	5.18
Benzo(k)fluoranthene (BkF)	BkFl	252	252	0	0	0	0
Benzo(e)pyrene (BeP)	BeP	252	252	7.57	8.32	9.94	8.12
Benzo(a)pyrene (BaP)	BaP	252	252	2.08	1.7	2.01	1.66
Perylene (Pe)	Pe	252	252	3.29	4.04	4.82	3.94
Indeno(1,2,3-cd)pyrene (IP)	IP	276	276	0.56	0.6	0.86	0.59
Dibenzo(ah)anthracene (DA)	DA	278	278	1.19	1.36	1.54	1.33
Benzo(ghi)perylene (BgP)	BgP	276	276	2.94	3.09	3.74	3.02
Total EPA priority PAHs				271	282	334	286
Total aromatic compounds (all alkyl and EPA PAH)				11725	12451	14616	13813

GMM = Gram Molecular Mass

QI = Quantitation Ion

4   Dispersant Effectiveness and Prediction

Environment Canada measured the dispersability using the swirling flask test. Results are shown in Table 14. This shows that ANS is relatively dispersible until it is highly weathered. This is considerably higher since the 1990's when it was measured at around 20% by the same method.

Table 14 Swirling Flask Dispersibility, Alaska North Slope 2015 (Hollebone, 2016)

	% Evaporative Mass Loss			
	0.00%	12.42	24.56	36.76
Swirling-Flask Dispersibility	45.9	51.4	51.6	4.9

Environment Canada also measured the dispersability using the baffled flask, results are shown in Table 15. These values appear to be rather high. The method by which these were done was based on the EPA proposal using an inappropriate colorimetric method that does not accurately measure oil, rather than the ASTM standard which has been in place for 20 years.

Table 15 Baffled Flask Dispersibility, Alaska North Slope 2015 (Hollebone, 2016)

	% Evaporative Mass Loss			
	0.00%	12.42	24.56	36.76
Baffled-Flask Dispersibility	97.2	96.2	81.6	74.8

Oil properties can be correlated with dispersant effectiveness to estimate the amount of oil dispersion. Such correlation could be used to indicate which oil properties, such as asphaltene content, might inhibit or facilitate oil dispersion.

5   Summary

The most important tools in oil spill planning and response is an understanding of oil spill behavior, whether derived directly or through accurate modeling and prediction. Decidedly, the most important data points are for oil spill emulsification, evaporation, chemical dispersibility and those (such as adhesion and distillation) that might be used to predict other countermeasures such as recovery and burning. This paper showed that the 2015 ANS data could be used to predict its behavior.

The 2015 emulsion formation predictions show that as a fresh oil, it will not produce a water-in-oil emulsion and that when highly weathered would still not produce an emulsion. This is quite different from older samples (pre-2001) which formed emulsions once weathered.

The dispersibility of the oil is 45% based on the standard swirling flask test. This implies the oil is dispersible until weathered over about 7 days.

The oil weathers to about 37% within the standard weathering period, which indicates that it is classified as a medium oil. Considering spill countermeasures, this percentage indicates that the oil will have low viscosity (<100 mPa.s) for a few days after spillage.

The chromatographic parameters such as TPH, show that ANS has a low TPH chromatographically and caution should be taken in using TPH values for environmental purposes such as biodegradation or toxicity. There are specialized chemical techniques to overcome these limitations.

The chemistry of the oil shows that it is abundant in alkanes and less so in PAHs and especially the more toxic PAHs (such as the multi-ring 5 or greater). This implies that the aquatic toxicity is moderate.

These numbers are consistent with the properties of a medium crude oil. It should be noted, however that the oil is much lighter than former oils from the same pipeline.

8.   References

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