Review of the 2019 Alaska North Slope Oil Properties Relevant to Environmental Assessment and Prediction

Prepared for

Prince William Sound Regional Citizens' Advisory Council (PWSRCAC)
Anchorage, Alaska

by

Merv Fingas
Spill Science
Edmonton, Alberta, Canada

March 2023

The opinions expressed in this PWSRCAC-commissioned report are not necessarily those of PWSRCAC. PWSRCAC Contract #5640.23.01

Non-Technical Summary

The Trans Alaska Pipeline System bringing Alaska North Slope (ANS) crude oil into Valdez carries different blends of the ANS oil depending on what oils are fed into the pipeline at Pump Station 1. After 2010, the blend of oils shifted dramatically with the absence of heavier crudes and the predominance of lighter oils. This had an influence on the possible environmental impacts of any spill of that oil, as well as on the effectiveness of countermeasures used to respond to a spill. Year by year, there continue to be changes in the composition of the ANS oil, more recently these changes are slight.

This paper is a summary of several oil parameters and the predicted spill behavior of a 2019 ANS sample provided to Environment and Climate Change Canada (Environment Canada). Environment Canada analysed the sample provided to them by PWSRCAC for environmental and physical parameters. As per a stipulation in the Prince William Sound tanker contingency plan, PWSRCAC receives an ANS crude sample at least every five years. PWSRCAC than has the oil samples analyzed for their physical and chemical properties.

The objectives of this report are to:

- Describe how the pertinent chemical and physical properties of this 2019 ANS sample affect mechanical (e.g., skimmers) and non-mechanical (e.g., dispersants) response methods;
- Describe how those properties affect the fate and transport of oil spilled in Prince William Sound; and
- Identify how the chemical properties of this sample have changed over time.

The 2019 sample of ANS oil was found to be similar to 2015 ANS oil, but different from samples in the more distant past. The essential parameters included in the analysis of the 2019 ANS crude are the oil viscosity, density, and emulsion formation tendency. The 2019 sample is somewhat lighter and less viscous than older samples. The environmental behavior parameters of evaporation, emulsification, and dispersibility were predicted in Environment Canada's analyses. The results show the 2019 ANS is a medium viscosity oil that does not form emulsions, is dispersible, and evaporates to an extent.

Composition Changes Effects on Oil Spill Countermeasures

The composition changes over time have generally made 2019 ANS oil lighter and less viscous making spilled ANS easier to physically recover and easier to pump. 2019 ANS crude is somewhat more dispersible and less prone to form water-in-oil emulsions.

Composition Changes Effects on the Environment

The composition changes over time have made spilled 2019 ANS oil somewhat more toxic to aquatic organisms. The decreasing viscosity and resin content has made spilled 2019 ANS oil less adhesive to shorelines.

Technical Data Summary

The essential 2019 ANS crude oil data are:

Table 1. Physical Properties - 2019

Test	Test Conditions		2019-11-22-5992.1 ANS Fresh (0%)	2019-11-22-5992.2.1 ANS W1 (10.79%)	2019-11-22-5992.3.1 ANS W2 (21.73%)	2019-11-22-5992.4.1 ANS W3 (33.04%)
Density (g/mL)	0 °C		0.8813 ± 0.0000	0.9099 ± 0.0000	0.9319 ± 0.0000	0.95 ± 0.0000
	15 °C		0.8700 ± 0.0000	0.8989 ± 0.0000	0.9208 ± 0.0000	0.9414 ± 0.0000
	0 °C	Shear (s^{-1}) 10			1149 ± 19	11880 ± 147
		Shear (s^{-1}) 100			859 ± 3	6008 ± 0.0000
Viscosity (mPas)		Shear (s^{-1}) 1000	25.0 ± 0.7	101 ± 0.4	527 ± 2	23.6 ± 0.9
	15 °C	Shear (s^{-1}) 1000	12.7 ± 0.2	37.5 ± 0.1	153 ± 1.0	909 ± 4
Water Content (% w/w)			0.2 ± 0.02	<0.1	<0.1	<0.1
Sulfur (% w/w)			1.0 ± 0.0	1.1 ± 0.0	1.2 ± 0.0	1.4 ± 0.0
Pour Point (°C)			-51 °C ± 1.5	-60 °C ± 0.0	-45 °C ± 1.5	-12 °C ± 0.0
Flash Point (°C)			<-19 °C	25 °C ± 0.0	82 °C ± 1.0	131 °C ± 1.0
Vapor Pressure (kPa)			45.8 ± 0.2			
Evaporation equation (at 15 °C)	A for %Ev = A + B ln t		-12.7684			
	B for %Ev = A + B ln t		6.3003			
Chemical dispersibility (15 °C)	Swirling Flask		43 ± 4	25 ± 2	12 ± 2	9 ± 4
	Baffled Flask		95 ± 2	93 ± 2	81 ± 3	86 ± 5

The 2019 data show that this sample is similar in density to that of the previous sample analyzed in 2015. Table 2 illustrates how key properties have changed over time.

Table 2 Brief History of Physical Property Values

Property	Value in 2019	Value in 2015	(all at 15°C) Value in 2012	Value in 2009
Density	0.8700	0.8639	0.8649	0.8626
Viscosity	12.7	9.9	14.2	13.1
Flash point	<-19 °C	NM		<-5
Sulfur content (%)	1.0 ± 0.0	0.9	0.93	2.6
Saturates (%w/w)	56	57.8		65.3
Aromatics (%w/w)	31	31.9		16.5
Resins (%w/w)	9 ± 0.4	6.5		14.7
Asphaltenes (%w/w)	4 ± 0.1	3.8		3.5

The essential environmental facts of the 2019 ANS sample are summarized in Table 3.

Table 3 Environmental Properties of the New ANS	
Evaporation	$\%Ev = (2.7 + .045T)\ln(t)$ T is temperature in Celsius t is the time in minutes
Emulsification	Does not form any type until heavily weathered Heavily weathered = entrained
Dispersibilty	43 ± 4% (Based on Swirling Flask test)

The origin and use of these predictions are illustrated in the text of the full report.

List of Acronyms and Definitions

ANS	Alaska North Slope - This usually refers to the crude oil mixture at the end of the pipeline
API	American Petroleum Institute
BTEX	Benzene, toluene, ethyl-benzene, and xylenes
ESTS	Emergencies Science and Technology Section – part of Environment and Climate Change Canada
EPA	U.S. Environmental Protection Agency
G/cm^3	Grams per cubic centimetre
GC	Gas chromatograph - This is a chemical analytical technique
PAHs	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
SARA	Saturates, aromatics, resins, and asphaltenes
TAH	Total aromatic hydrocarbons
TPH	Total petroleum hydrocarbons
TSH	Total saturate hydrocarbons
VOCs	Volatile organic compounds

Acknowledgements

The author thanks Austin Love of the Prince William Sound Regional Citizens' Advisory Council for his help and guidance.

Table of Contents

Non-technical Summary ii
Technical Data Summary iii
List of Acronyms v
Acknowledgements vi

1. Introduction 1
   1.1 Background 1
   1.2 Oil Properties and North Slope Crude 1
   1.3 A Summary of Oil Composition and Behavior 1
      1.3.1 Oil Properties 2
      1.3.2 Behavior of Oil 11

2. Summary of ANS Behavior 13
   2.1 Oil Evaporation 14
   2.2 Emulsification 15

3. Chemistry of ANS 17

4. Dispersant Effectiveness and Prediction 23

5. Summary 23

6. References 25

List of Tables

1 Physical Properties - 2019 iii
2 Brief History of Physical Property Values iv
3 Environmental Properties of 2019 ANS iv
4 Typical Viscosity Comparison 3
5 Typical Density Comparison 6
6 Typical Flash Point Comparison 7
7 Typical Adhesion Comparison 10
8 Emulsion Formation 16
9 GC Detectable Hydrocarbons 17
10 Hydrocarbon Groups Analysis 18
11 n-Alkanes 20
12 PAHs and Alkyl PAHs 21
13 Biomarkers 22
14 Swirling and Baffled Flask Dispersibility 23

List of Figures

1 History of viscosity measurements over 15 Years 4
2 History of density measurements over 15 Years 5
3 History of percent distilled at 180°C measurements 8
4 History of sulfur content of fresh ANS oil 9
5 The evaporation of the 2019 ANS sample 14

1 Introduction

1.1 Background

The overall objective of this paper is to provide properties and environmental prediction information on the 2019 sample of ANS crude oil. Additional objectives include:

- Describing how the pertinent chemical and physical properties of this 2019 ANS sample affect mechanical and non-mechanical response methods;
- Describing how those properties affect the fate and transport of oil spilled in Prince William Sound; and
- Identifying how the chemical properties of this sample have changed over time.

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. The characteristics of the fields vary and thus, as they are blended into Pump Station 1 at the head of the trans-Alaska 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 in 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 2019, a new sample was drawn and the properties were measured and reported by Environment Canada (2022). Table 1 gives these properties (ESTS, 2022). Comparison shows that the 2019 sample is about the same as the 2013-2015 samples 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 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.

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 2019 ANS oil can be compared to the old ANS oils and from Figure 1 it can be seen that the 2019 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 cP)

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%)
2019 ANS	12.7	153 (22%)	900 (33%)
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

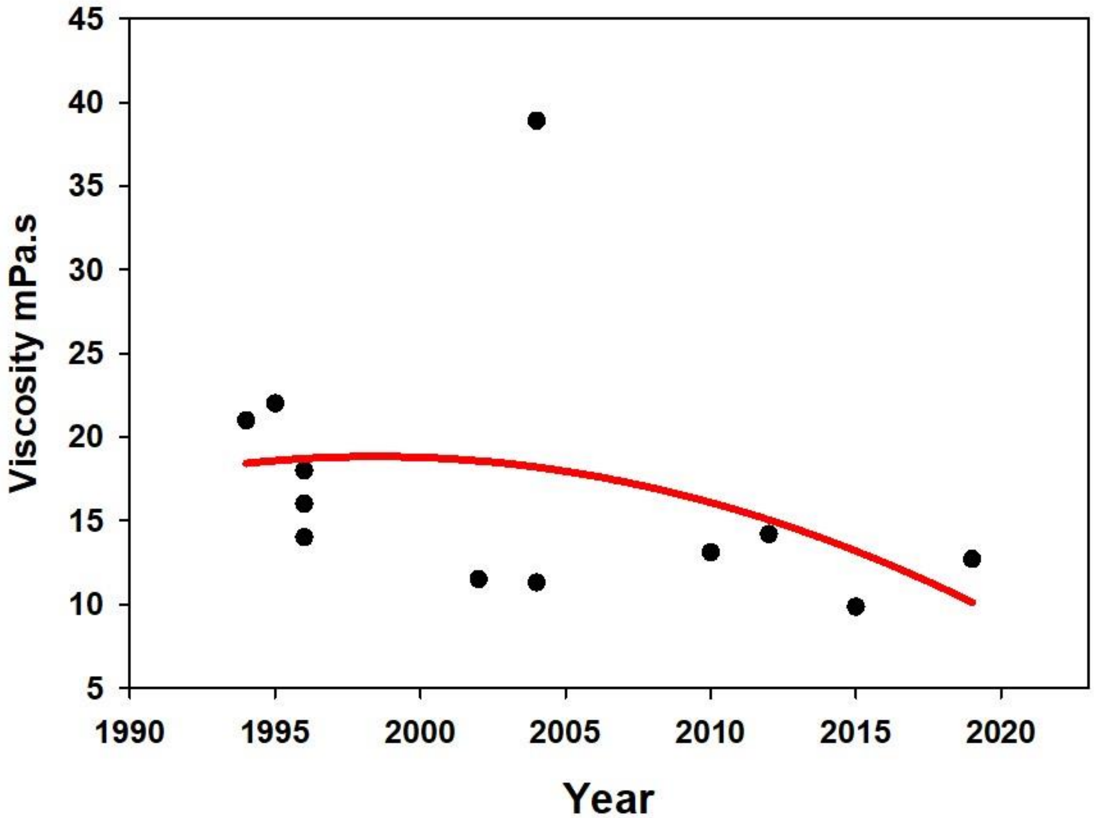

Figure 1. History of the viscosity measurements.

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^oC 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 with only 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 2019 sample density to the old data, one can examine Figure 2. This shows that the 2019 sample is quite different from the very old samples, but similar to the last two 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 17 years. In the past few years, there is some variance in density which is considered to be minor. Sample density is indicative of composition and the lighter or less dense that an oil is, the easier it is to clean up.

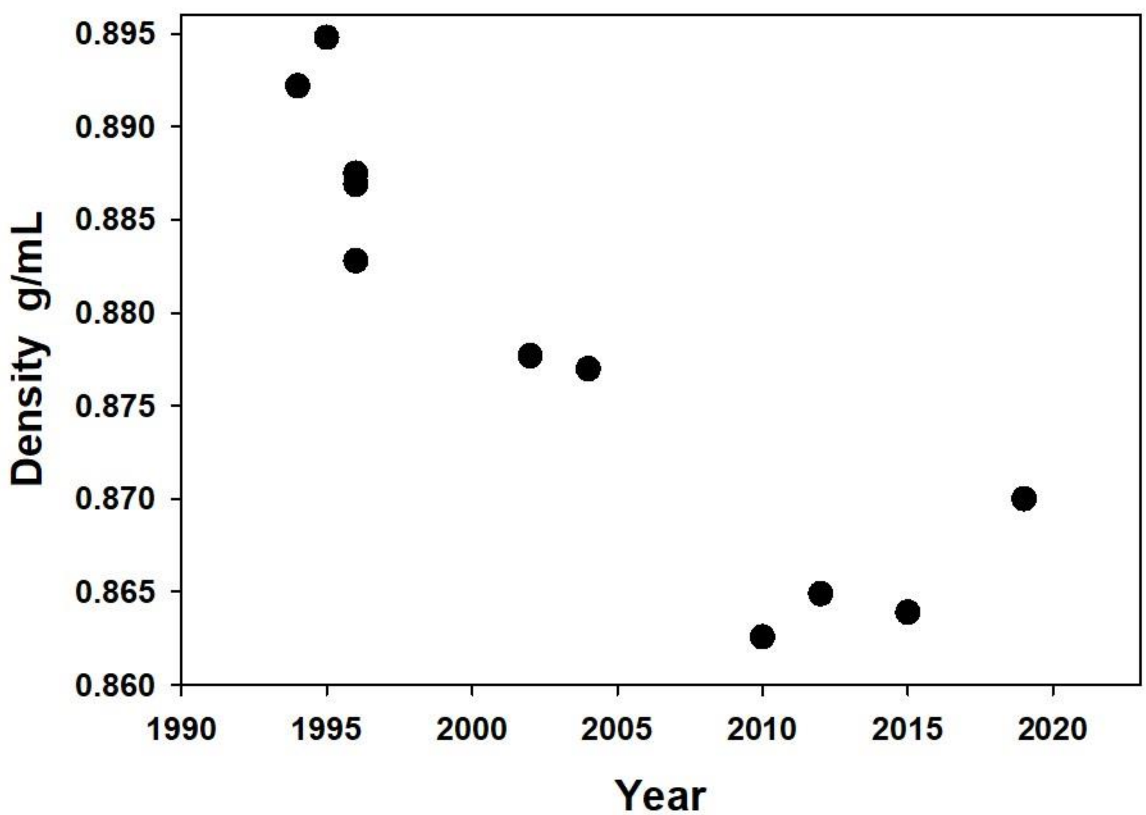

Figure 2. History of the density measurements.

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 15°C, 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%)
2019 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

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)

(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%)
ANS	-19	82 (22%)	131 (33%)
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

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 with previous years' samples.

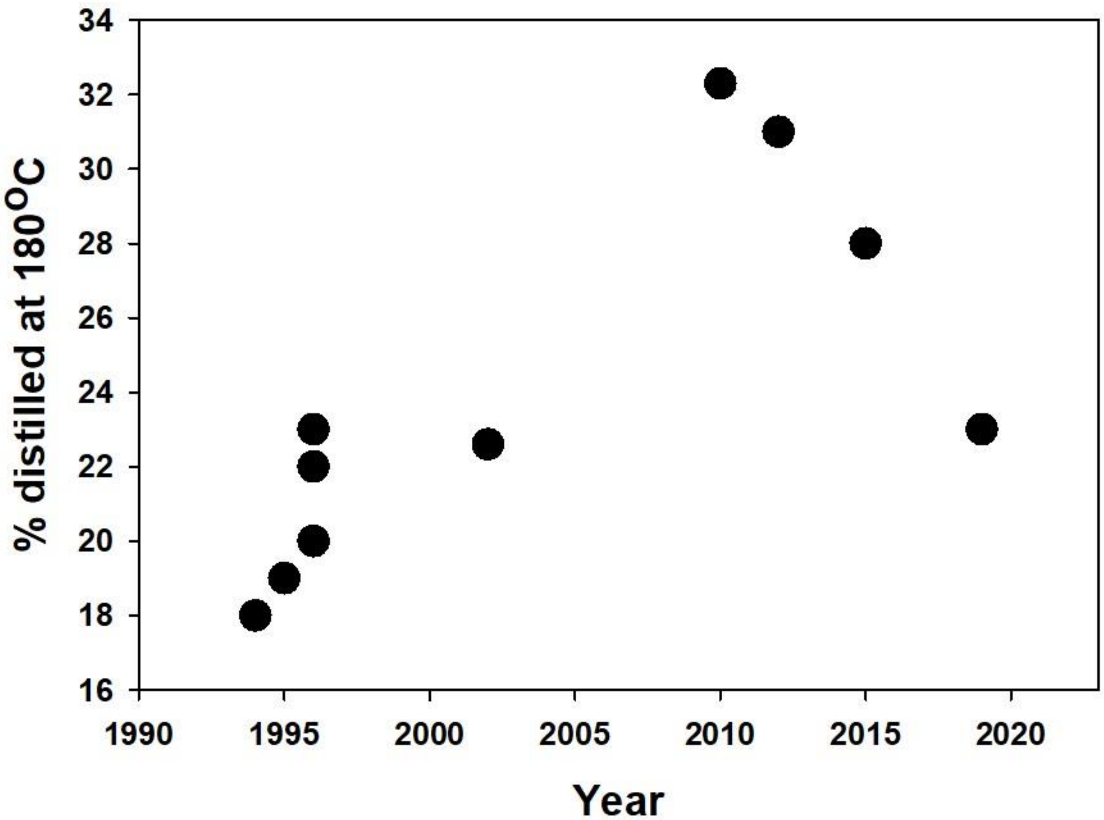

Figure 3. History of the percent distilled at 180°C.

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 17 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.

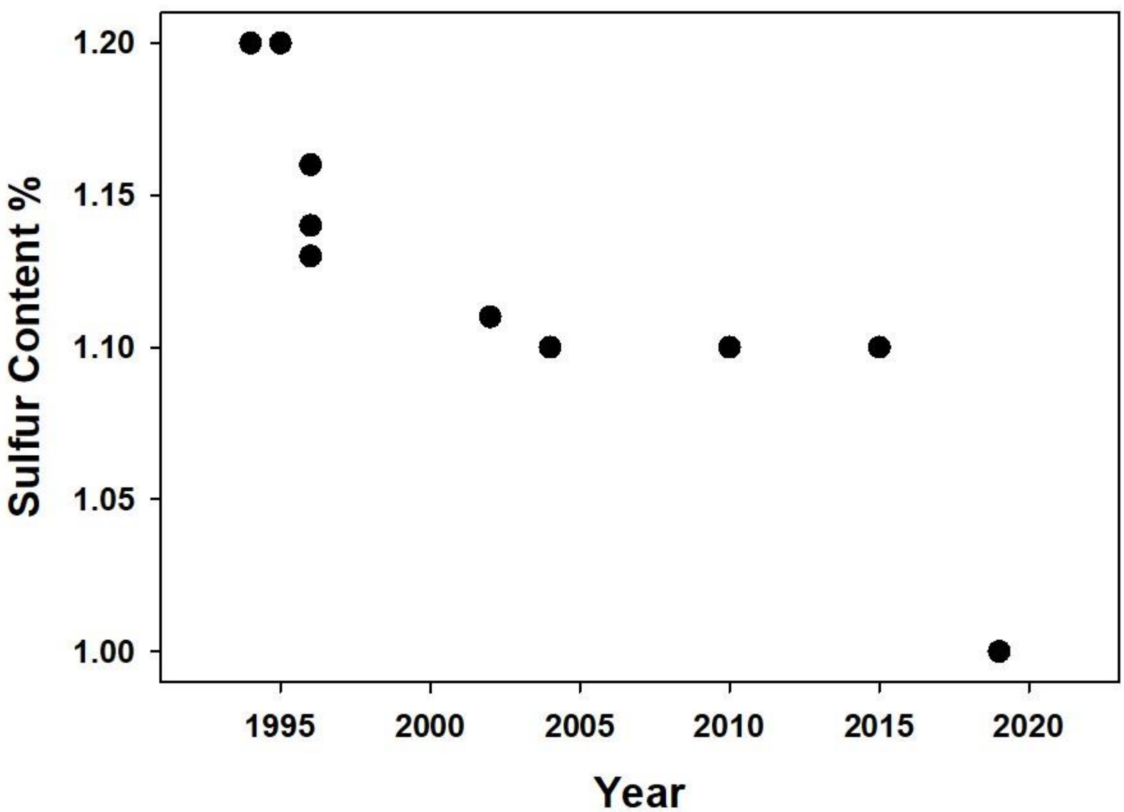

Figure 4. The history of the sulfur content of fresh ANS oil.

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 the last 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 in 2015 but not in 2019. 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 (2019) Typical Adhesion Comparison

(data in g/m^2)

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. If 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 at 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 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 heavy fuel 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 (ESTS, 2022). 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:

$$\%Ev = (2.7 + .045T)\ln(t) \quad (1)$$

Where %Ev is the percent evaporated at T °C

and t is the time in minutes.

This is an empirical equation derived from controlled experiments. Figure 5 shows the predicted evaporation at different temperatures. This shows that the 2019 ANS would evaporate significantly at normal ambient temperatures within a few days.

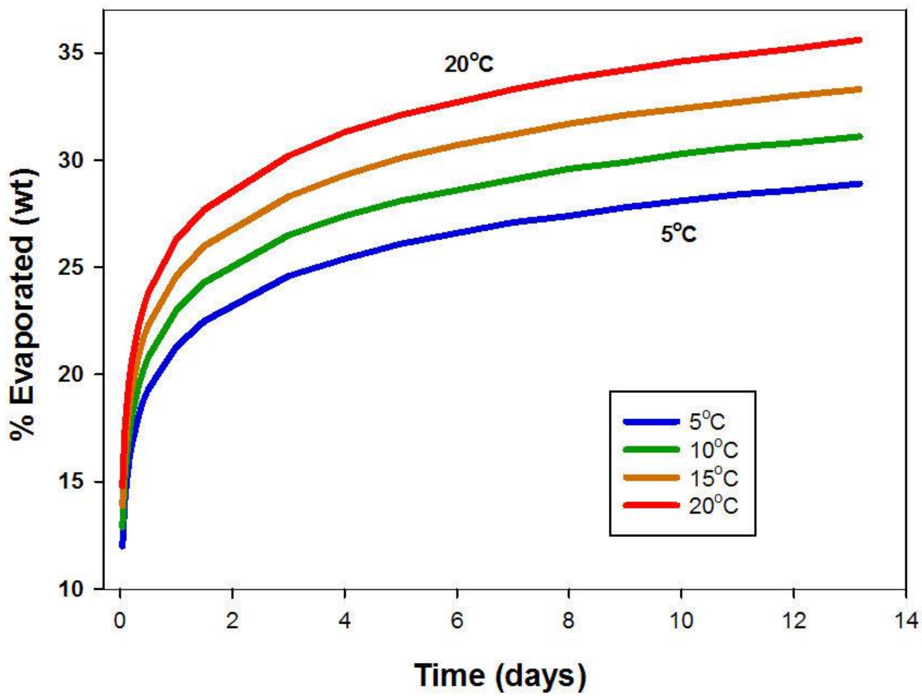

Figure 5. The evaporation of the 2019 ANS Sample

2.2 Emulsification

Water-in-oil emulsions sometimes form after oil products are spilled. These emulsions, often called “chocolate mousse” or “mousse” by oil spill workers, can make the cleanup of oil spills very difficult. When water-in-oil emulsions form, the physical properties of oil changes dramatically. As an example, stable emulsions contain from 60 to 80% water, thus expanding the spilled material from two to five times the original volume. Most importantly, the viscosity of the oil typically changes from a few hundred mPa·s to about 100,000 mPa·s, an increase by a factor of 500–1000. A liquid product is changed into a heavy, semisolid material. These emulsions are difficult to recover with ordinary spill recovery equipment. A test of the emulsification of this 2019 sample of ANS showed that it does not produce any form of stable emulsion. This is good news, as it shows that the oil would be easy to recover even after moderate weathering. However, highly weathered oil can retain entrained water. Table 8 shows the results.

Table 8 Emulsion Formation, Alaska North Slope 2019 (ESTS, 2022)					
Emulsion	**Units**	2019-11-22- **ANS Fresh (0%)**	2019-11-22-5992.2.1 **ANS W1 (10.79%)**	2019-11-22-5992.3.1 **ANS W2 (21.73%)**	2019-11-22-5992.4.1 **ANS W3 (33.04%)**
Visual stability 15 °C (1st day)		Distinct oil water layers	Distinct oil water layers	Distinct oil water layers	Oil water emulsion
Complex modulus 15 °C (1st day)	Pa	N/A	N/A	N/A	15.4 ± 4.9
Storage Modulus 15 °C (1st day)	Pa	N/A	N/A	N/A	1.49 ± 2.09
Tan Delta (V/E) 15 °C (1st day)		N/A	N/A	N/A	15.6 ± 11.7
Complex dynamic viscosity (1st day)	mPa.s	N/A	N/A	N/A	2448 ± 778
Water Content (1st day)	%w/w	N/A	N/A	N/A	18.9 ± 0.6
Visual stability 15 °C (8th day)		Unstable	Unstable	Unstable	**Entrained**
Complex modulus 15 °C (8th day)	Pa	N/A	N/A	N/A	7.09 ± 0.96
Storage Modulus 15 °C (8th day)	Pa	N/A	N/A	N/A	0.36 ± 0.23
Tan Delta (V/E) 15 °C (8th day)		N/A	N/A	N/A	29.6 ± 21.9
Complex dynamic viscosity (8th day)	mPa.s	N/A	N/A	N/A	1129 ± 153
Water Content (8th day)	%w/w	N/A	N/A	N/A	5.7 ± 0.4

The parameters in Table 8 are standard characterizations of heavy oils or emulsions, explanations can be found in rheological introductions (Malvern, 2016). The new sample of ANS doesn't form stable emulsions, however highly weathered samples can retain water by viscosity forces.

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 100,000 compounds in an oil. In the future, this number will no doubt rise significantly.

The gas chromatographic, or GC, characteristics of 2019 ANS oil are shown in Table 9.

Table 9 GC-Detectible Hydrocarbons, Alaska North Slope 2019 (ESTS, 2022)

		Oil (% weathered)			
Category	**Units**	**ANS Fresh (0%)**	**ANS W1 (10.79%)**	**ANS W2 (21.73%)**	**ANS W3 (33.04%)**
TPH	mg/g oil	663	681	657	663
TSH	mg/g oil	428	465	422	410
TAH	mg/g oil	235	215	235	252
Resolved peaks (F3)	mg/g oil	169	141	153	105
TSH/TPH (%)	(%)	64.6	68.4	64.2	61.9
TAH/TPH (%)	(%)	35.4	31.6	35.8	38.1
Resolved Peaks/TPH (%)	(%)	27.8	20	21.9	16
TPH fractions (%)					
TPH F1 (<n-C10)	(%)	11.6	10.8	3.01	0
TPH F2 (>n-C10-n-C16)	(%)	25.3	28	27.8	16.8
TPH F3 (>n-C16-n-C34)	(%)	48.8	48.2	53.8	64.9
TPH F4 (>n-C34)	(%)	14.3	13	15.4	18.3

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 663 mg (out of 1000). This amounts to 66%. The remainder of the oil did not make it through the chromatographic column. This is very important in considering an oil as any measurements made of it are only analyzing 66%. 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/TPH 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 environmental scientist. 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 composition of the latest fraction of ANS oil by TPH fraction, this is another bulk classification which relates the chemistry of oil to chromatographic analysis.

Table 10 Hydrocarbon Groups Analysis, Alaska North Slope 2019 (ESTS, 2022)

Customer sample info.	Units	ANS Fresh (0%)	ANS W1 (10.79%)	ANS W2 (21.73%)	ANS W3 (33.04%)
TPH	mg/g oil	663	681	657	663
TSH	mg/g oil	428	465	422	410
TAH	mg/g oil	235	215	235	252
Resolved peaks (F3)	mg/g oil	169	141	153	105
TSH/TPH (%)	(%)	64.6	68.4	64.2	61.9
TAH/TPH (%)	(%)	35.4	31.6	35.8	38.1
Resolved Peaks/TPH (%)	(%)	27.8	20	21.9	16
TPH fractions (%)					
TPH F1 (<n-C10)	(%)	11.6	10.8	3.01	0
TPH F2 (>n-C10-n-C16)	(%)	25.3	28	27.8	16.8
TPH F3 (>n-C16-n-C34)	(%)	48.8	48.2	53.8	64.9
TPH F4 (>n-C34)	(%)	14.3	13	15.4	18.3

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.

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 12. Table 13 shows the biomarkers present in ANS oil. Biomarker compounds are typically used to trace unknown oil spill samples.

Table 11 n-Alkanes, Alaska North Slope 2019 (ESTS, 2022)				
μg/g	ANS Fresh	ANS W1	ANS W2	ANS W3
% Evaporative Mass Loss	0%	-10.79%	-21.73%	-33.04%
n-C9	4,324	4,401	1,610	1
n-C10	4,091	4,348	3,521	2
n-C11	3,667	3,958	3,932	58
n-C12	3,340	3,692	3,807	1,192
n-C13	3,132	3,525	3,676	2,901
TMD	729	853	880	815
n-C14	2,919	3,224	3,388	3,666
n-C15	2,476	2,655	2,853	3,485
n-C16	2,206	2,400	2,565	3,227
TMP	1,111	1,251	1,324	1,548
n-C17	2,366	2,323	2,461	3,127
Pristane	1,106	1,181	1,253	1,621
n-C18	1,860	2,000	2,155	2,780
Phytane	1,030	1,143	1,316	1,661
n-C19	1,720	1,859	1,982	2,590
n-C20	1,614	1,743	1,857	2,439
n-C21	1,523	1,659	1,767	2,278
n-C22	1,459	1,578	1,682	2,195
n-C23	1,387	1,519	1,606	2,020
n-C24	1,271	1,397	1,531	1,927
n-C25	1,087	1,196	1,266	1,743
n-C26	1,104	1,232	1,305	1,655
n-C27	829	1,026	1,009	1,269
n-C28	650	759	739	919
n-C29	518	620	651	809
n-C30	503	516	605	729
n-C31	398	505	529	651
n-C32	310	370	398	479
n-C33	243	322	343	418
n-C34	191	269	282	332
n-C35	184	260	236	322
n-C36	146	209	201	244
n-C37	115	168	166	218
n-C38	98	144	144	176
n-C39	72	88	97	120
n-C40	54	63	68	87
Total n-alkanes	49,834	54,455	53,204	49,705

Table 12 PAHs and alkyl PAHs, Alaska North Slope 2019 (ESTS 2022)					
	Oil	Fresh	ANS W1	ANS W2	ANS W3
Alkylated PAHs	Weathered %		-10.79%	-21.73%	-33.04%
Chrysene	C0-N	504	603	649	65.9
	C1-N	1489	1823	2002	1118
	C2-N	2150	2619	2931	2616
	C3-N	1823	2230	2514	2589
	C4-N	1049	1216	1325	1478
	Sum	7016	8489	9420	7867
Phenanthrene	C0-P	165	193	220	248
	C1-P	533	607	691	776
	C2-P	608	701	808	902
	C3-P	508	552	641	702
	C4-P	250	286	301	350
	Sum	2063	2341	2661	2978
Dibenzothiophene	C0-D	108	127	145	160
	C1-D	316	368	422	469
	C2-D	471	566	653	753
	C3-D	476	495	594	695
	Sum	1371	1557	1814	2077
Fluorene	C0-F	65.5	77.9	89.3	91.3
	C1-F	253	298	362	367
	C2-F	420	455	542	593
	C3-F	404	479	506	590
	Sum	1143	1310	1499	1642
Fluoranthene	C0-Fl	2.38	3.01	2.81	3.51
	C1-Fl	58.8	64.5	67.4	86.1
	C2-Fl	94.8	105	128	137
	C3-Fl	118	130	160	165
	C4-Fl	82.5	101	109	118
	sum	356	403	468	509
Benzonaphthothiophene	C0-B	37.2	43.4	49.7	54.3
	C1-B	163	164	208	217
	C2-B	219	242	280	309
	C3-B	200	213	249	274
	C4-B	110	123	141	151
	Sum	729	786	928	1006
Chrysene	C0-C	29.7	34.9	39.2	43.7
	C1-C	57.8	61.6	71.7	79
	C2-C	78.4	91.4	101	113
	C3-C	76.6	90.6	104	116
	Sum	242	278	316	352
Total alkylated PAHs		12921	15165	17106	16432
Other Priority PAHs					
Biphenyl (Bph)	Bph	115	138	154	118
Acenaphthylene (Acl)	Acl	11.3	13.5	15.1	14.2
Acenaphthene (Ace)	Ace	12.7	15.2	17.1	16
Anthracene (An)	An	5.91	6.96	7.91	8.42
Fluoranthene (Fl)	Fl	4.22	4.82	6.1	6.89
Pyrene (Py)	Py	15.2	17.2	19.9	21.7
Benz(a)anthracene (BaA)	BaA	1.92	1.72	2.35	3.43
Benzo(b)fluoranthene (BbF)	BbF	4.75	5.43	6.37	7
Benzo(k)fluoranthene (BkF)	BkF	0	0	0	0
Benzo(e)pyrene (BeP)	BeP	8.58	9.38	11.76	12.38
Benzo(a)pyrene (BaP)	BaP	1.62	2.02	2.28	2.71
Perylene (Pe)	Pe	6.73	7.33	8.79	10.1
Indeno(1,2,3-cd)pyrene (IP)	IP	0.61	0.66	0.87	0.84
Dibenzo(ah)anthracene (DA)	DA	1.31	1.35	1.56	1.66
Benzo(ghi)perylene (BgP)	BgP	3	3.31	3.63	3.93
Total EPA priority PAHs		193	227	258	227
Total aromatic compounds		13114	15392	17364	16659

Table 13 Biomarker compounds, Alaska North Slope 2019 (ESTS, 2022)				
	ANS Fresh	ANS W1	ANS W2	ANS W3
Sample weathering %	**0%**	**-10.79%**	**-21.73%**	**-33.04%**
Biomarker compounds	µg/g oil	µg/g oil	µg/g oil	µg/g oil
C21 terpane	15.8	18.6	19	24.1
C22 terpane	6.57	7.63	7.75	10.8
C23 terpane	40.4	46.2	47.9	61.1
C24 terpane	26.3	30.1	31	38.8
C27 Ts	14.7	19	21.5	25.5
C27 Tm	29.3	33.8	35.5	44.7
C29ab hopane	68.8	78.7	82.3	103
C30ab hopane	93.9	106	112	143
C31(S) hopane	38.5	43.3	46	58.5
C31(R) hopane	30.7	35.1	36.6	46.1
Gammacerane	9.71	10.4	73	13
C32(S) hopane	30.1	34	35	44.3
C32(R) hopane	21.5	24.8	25.3	32.1
C33(S) hopane	22.2	25.5	26.3	33.2
C33(R) hopane	15.3	17.7	18.5	23.2
C34(S) hopane	17.2	19.8	20.6	25.8
C34(R) hopane	10.7	12.4	13	17.5
C35(S) hopane	17.8	20.7	21.6	27.3
C35(R) hopane	14.1	16.6	17.5	22.2
C27abb steranes	139	158	160	198
C28abb steranes	117	132	139	171
C29abb steranes	150	170	176	228
Total	930	1061	1165	1391
Diagnostic Ratios				
C23/C24	1.53	1.54	1.55	1.57
C23/C30	0.43	0.43	0.43	0.43
C24/C30	0.28	0.28	0.28	0.27
C29/C30	0.73	0.74	0.73	0.72
C31(S)/C31(R)	1.25	1.23	1.26	1.27
C32(S)/C32(R)	1.4	1.37	1.38	1.38
Ts/Tm	0.5	0.56	0.61	0.57
C27abb / C29abb	0.93	0.93	0.91	0.87
C30/(C31+C32+C33+C34+C35)	0.41	0.41	0.34	0.42

4 Dispersant Effectiveness and Prediction

Environment Canada measured the dispersability using the swirling flask test. Results are shown in Table 14. This shows that 2019 ANS is relatively dispersible until it is highly weathered. This is considerably higher since the 1990s when it was measured at around 20% by the same method. This means the 2019 ANS oil is more dispersible than previous ANS crude samples.

Table 14	Chemical dispersibility at 15°C			
	ANS Fresh (0%)	ANS W1 (10.79%)	ANS W2 (21.73%)	ANS W3 (33.04%)
Swirling Flask	43 ± 4	25 ± 2	12 ± 2	9 ± 4
Baffled Flask	95 ± 2	93 ± 2	81 ± 3	86 ± 5

Environment Canada also measured the dispersability using the baffled flask, results are also shown in Table 14.

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 tool 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 2019 ANS data from Environment Canada could be used to predict its behavior.

The 2019 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 43% based on the standard swirling flask test. This implies the oil is dispersible until weathered over about 1 day.

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. This is important as spill countermeasures effectiveness deteriorates rapidly with increasing viscosity. The 2019 ANS spilled oil can be recovered easier than older ANS oils.

Further, the fate and transport of the 2019 ANS oil would be affected. The lesser viscosity of the 2019 oil means that spills will spread further and faster than they would have in the past. The Exxon Valdez spill was of the older type of crude oil, and would have a different fate than if the oil were of the newer type. The oil would have moved out of Prince William Sound faster and spread into the Gulf of Alaska faster.

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.

The 2019 ANS crude properties are consistent with the properties of a medium viscosity crude oil. It should be noted, however that the oil is much lighter than former oils from the Trans Alaska Pipeline System.

8. References

ESTC (Environmental Technology Centre), World Catalogue of Oil Properties, WWW.ETC-CTE.ec.gc.ca, 2016.

ESTS Report No. 2022-Rep_Alaska North Slope Analysis, ESTS#5992, 2022.

Fingas, M., "Introduction to Oil Chemistry and Properties", Ch. 2 in *Handbook of Oil Spill Science and Technology*, M. Fingas, Editor; John Wiley and Sons Inc., NY, pp. 53-77, 2015.

Fingas, M.F., Z. Wang, B. Fieldhouse, and P. Smith, "The Correlation of Chemical Characteristics of an Oil to Dispersant Effectiveness", in *Proceedings of the Twenty-Sixth Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 679-730, 2003.

Fingas, M. and B. Fieldhouse, "Studies on Crude Oil and Petroleum Product Emulsions: Water Resolution and Rheology", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 333, pp. 67-81, 2009.

Fingas, M. and B. Fieldhouse, "Studies on Water-in-oil Products from Crude Oils and Petroleum Products," Mar. *Pollut. Bull*., Vol: 64, pp. 272-283, 2011.

Hollebone, B., *Physical and Chemical Properties of Alaskan North Slope [2012] Crude Oil*, a report for PWS RCAC, 2013.

Hollebone, B., *Physical and Chemical Properties of Alaskan North Slope [2015] Crude Oil*, a report for PWS RCAC, 2016.

International Petroleum Encyclopedia, PenWell Books, Tulsa, OK, 2015

Malvern, http://www.iesmat.com/iesmat/upload/file/Malvern/Productos-MAL/REO-A%20basic%20introduction%20to%20rheology.pdf, accessed June 2016

Wang, Z., B.P. Hollebone, M. Fingas, B. Fieldhouse, C. Yang, M. Landriault, and S. Peng, “Characteristics of Spilled Oils, Fuels, and Petroleum Products: I Composition and Properties of Selected Oils”, U.S. Environmental Protection Agency, EPA/600/R-03/072, National Exposure Laboratory, Atlanta, GA, 2004.