

# **Hydrocarbon Research Internship**

Prince William Sound

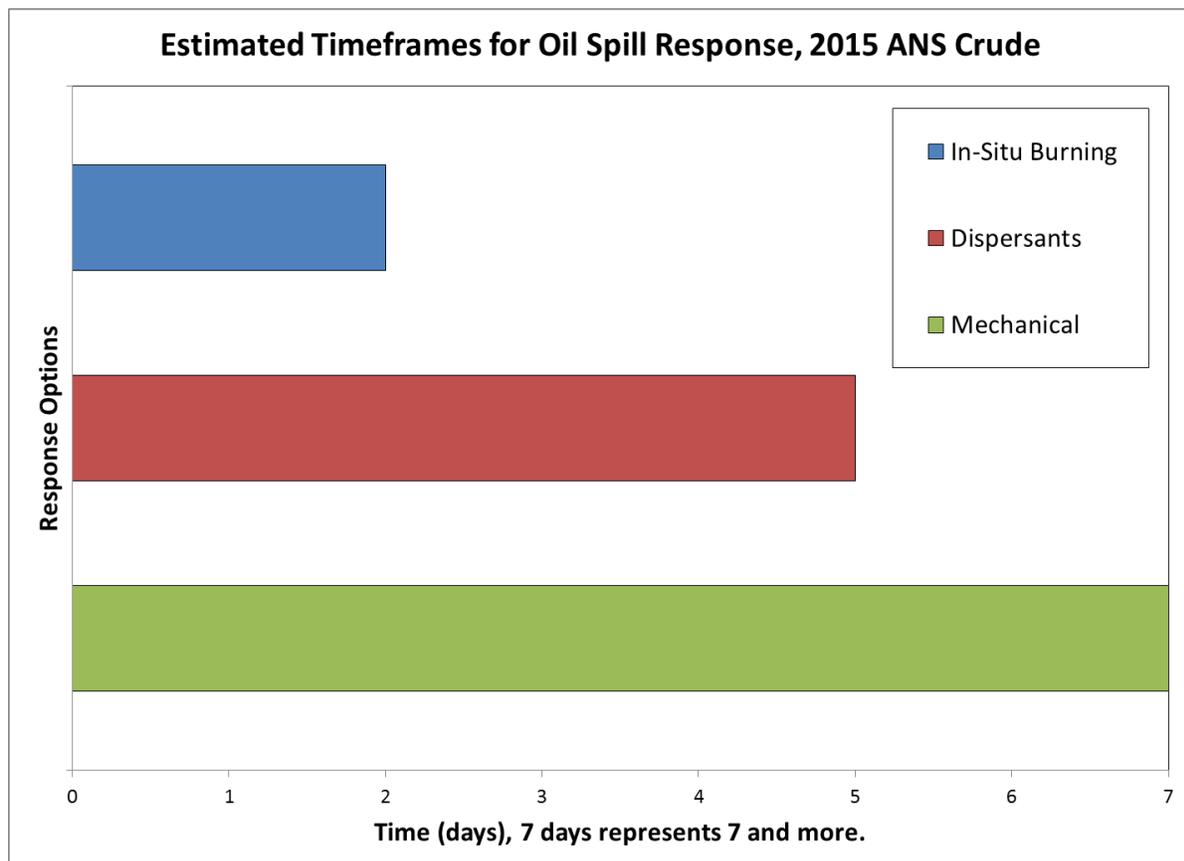
Regional Citizen's Advisory Council

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**Summary:** Samples of Alaska North Slope crude oil (ANS) were obtained by the Prince William Sound Regional Citizen's Advisory Council in 2015 and sent to Environment Canada for analytical testing. Testing results indicated no major changes in ANS properties from the last time ANS underwent testing in 2013. The 2015 sample did not emulsify under lab conditions, except in cases of extreme weathering. Based on testing results, approximately 12% by mass of ANS will evaporate within 40 minutes immediately after a spill occurs, 25% will evaporate within 24 hours, and 36% will evaporate within 30 days. The viscosity and density of the 2015 sample both increased as evaporation occurred. Scientific literature indicates reduced dispersant effectiveness for ANS at viscosities exceeding 1000 cP. Based on testing results, this could take anywhere from 2 - 5 days for the 2015 sample depending on weather conditions. As a general rule, crude oil having a density heavier than 20 degrees API is considered unignitable for in-situ burning. Based on test results this might take 1-2 days for the 2015 sample. Test results also indicated mechanical recovery will likely not be compromised provided appropriate skimming equipment is used under workable weather conditions. The figure below illustrates general rules of thumb regarding oil spill response methods for ANS, based on 2015 testing results from Environment Canada. Colder temperatures could shorten windows of opportunity, especially for burning and dispersants. All spill parameters are weather dependent. These timeframes are merely estimates and actual response times will vary depending on environmental conditions.



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## 1. Crude Oil Chemical and Physical Properties

A property is any characteristic that can be observed or measured. For example, a crude oil's color can be observed and wax content and sulfur content can be measured. Therefore, these characteristics are properties of crude oil. Common crude oil properties tested in a lab are chemical composition, interfacial tension, flash point, viscosity, and density. In order to further illustrate how crude oil's physical and chemical properties may be broken down, a brief discussion of each follows. Two main properties - viscosity and density - are widely considered as being the best indicators for how effective oil spill response technologies will be.

### 1.1 Chemical Composition

Crude oil is a mixture of hundreds of different kinds of molecules, and these molecules are roughly divided into four categories: saturates, aromatics, resins (polar), and asphaltenes (SARA). SARA content is the distribution of crude oil within each category by percent weight. Saturates are typically light weight, straight chained hydrocarbons and make up the majority of crude oil. Aromatics are identified by a chemical bond called a benzene ring, and are considered to be highly toxic. Asphaltenes and resins are typically heavier molecules and increase a crude oil's tendency to form emulsions (1, p.93). Figure 1 illustrates these different types of chemicals. All figures are located in Appendix A and Tables in Appendix B, attached to this report.

Chemical composition is important because it determines what a crude oil's physical properties are. No two crude oils have the exact same chemical composition. This is because

crude oil varies from region to region based on the geological formation, and oil gradually changes over time as it is produced from a well. Typically, oil becomes heavier and more viscous as a reservoir is depleted.

## **1.2 Examples of Physical Properties - Interfacial Tension and Flash Point**

Different fluids, for instance oil and water, are separated at a boundary called an interface. Interfacial tension describes how much resistance exists between separating two fluids at their interface, and is usually given in milli-Newtons per meter (mN/m). When interfacial tension is taken between liquid and air, it is referred to as surface tension (2, p.6). Low interfacial tension results in oil spreading out more over water and being able to form smaller droplets in water. In fact, dispersants work by lowering oil's interfacial tension to that of surrounding sea conditions, which allows sea energy to disperse oil into the water column (3, p.12). Interfacial tension usually varies only a small amount between different crude oils (4, p.3).

Flash point is "the lowest temperature at which a substance can vaporize to form an ignitable mixture" (5, p.11). Flash point is given in degrees Celsius (°C) or Fahrenheit (°F). It is an important property for safety considerations such as during cleanup or handling operations. It also influences how easily the oil will ignite during in-situ burning. Because flash point describes how readily the oil vaporizes, it has no appreciable effect on how oil behaves as a fluid during an oil spill.

### 1.3 Two Critical Properties - Viscosity and Density

As previously mentioned, two properties are used as major indicators to predict how an oil will behave during a spill and how effective any particular cleanup technology will be.

Viscosity is a fluid property which describes how much resistance internal layers of fluid encounter when flowing past each other. Its units are centi-Poise (cP), or milli-Pascal seconds (mPa-s) - which is equivalent to cP. An example of a high viscosity fluid is molasses, which has a viscosity of roughly 10,000 cP. For comparison, water has a viscosity of 1 cP. Centi-Poise is actually used when referring to dynamic or absolute viscosity. Another way of stating viscosity is kinematic viscosity, which is dynamic viscosity divided by density, with units of centi-Stokes (cSt). What's different between dynamic viscosity and kinematic viscosity is that the first measures a fluid's absolute resistance to flow, and the other is a derived quantity which describes a fluid's resistance to flow under gravity.

Density describes the mass per unit volume of a substance. Typical units are grams per cubic centimeter ( $\text{g}/\text{cm}^3$ ). Often, density is expressed as some fraction of the density of fresh water. This is called specific gravity. Oil floats on top of water because it is less dense than water, which is why specific gravity is a desired value. Oil industries also have a way of expressing crude oil density called API gravity, which is given in units of degrees API ( $^{\circ}\text{API}$ ). API gravity is somewhat counter-intuitive; higher  $^{\circ}\text{API}$  values correspond with less dense oils and smaller  $^{\circ}\text{API}$  values mean denser oils. In 2015 Alaska North Slope crude oil (ANS) had an API gravity of 31, and was designated as a 'light' to 'medium' crude oil - see Table 1 (6, p.4).

## **2. Overview of Weathering Processes**

Despite what crude oil properties may be while oil is being transported, once oil is spilled into the marine environment its properties will change with time. Weathering processes act upon oil once it is spilled and cause changes to the oil's chemical composition and physical properties. Such weathering processes include evaporation, emulsification, dissolution, microbial oxidation, and photo-oxidation. Two critical weathering processes are evaporation and emulsification.

### **2.1 Evaporation**

Evaporation occurs when oil is exposed to open air and lighter molecules escape into the atmosphere. Evaporation occurs very rapidly immediately after an oil spill occurs, and gradually decreases with time. This may be observed and measured in a lab by allowing a sample of crude oil to evaporate under controlled conditions, and taking sample weights periodically to see how much is lost to evaporation. Figure 2 represents evaporation curves for various kinds of petroleum, with lighter petroleum evaporating more due to higher amounts of lighter molecules. Since evaporation removes lighter molecules and leaves heavier ones, evaporation increases density and viscosity (7, p.74).

### **2.2 Emulsification**

When crude oil is spilled in water, energy from waves and the sea can cause oil to uptake tiny water droplets. Once they penetrate, these water droplets may stabilize inside oil due to viscous entrainment and surfactant-like action from asphaltenes and resins. Crude oil

exposed to sea energy will likely uptake water, and if an emulsion forms the water will not separate out very quickly. Emulsification acts to increase spill volume (through increasing water content), oil viscosity, and density. A stable water-in-oil emulsion can contain anywhere from 60-80% water by weight - see Table 2 (1, p.93). Emulsified crude is sometimes called mousse and can become a highly viscous, almost semi-solid material. Mousse was encountered during the Exxon Valdez oil spill cleanup. While freshly spilled oil may not form an emulsion immediately, once evaporation occurs and asphaltene and resin concentrations increase, the oil has a greater tendency to quickly emulsify (3, p.6).

### **2.3 Other Weathering Processes**

Other weathering processes include dissolution, photo oxidation, and microbial degradation, and are not as important in terms of predicting oil spill behavior. Dissolution is loss of water-soluble components, such as toxic aromatic compounds, into the water column. Photo-oxidation and microbial degradation fall under oxidative processes which break down and transform hydrocarbons. Photo oxidation could potentially be heightened by longer periods of sunlight during Alaska summers.

Microbial degradation acts to breakdown crude oil into different substances. When oil is separated into tiny droplets, biodegradation can occur at a faster rate because more surface area is available for micro-organisms to attach, whereas tar balls and mousse degrade extremely slowly (8, p.77). It is thought chemical dispersants speed up natural microbial degradation; however, evidence from dispersant research does not reinforce such claims. Another way microbial degradation has been altered is through fertilizers. Fertilizer additives

used during Exxon Valdez spill cleanup activities reportedly increased biodegradation by 3 - 5 times (7, p.83).

### **3. Oil Properties and Spill Response Technologies**

When crude oil is weathered by evaporation and emulsification, clean-up technologies gradually lose effectiveness. Eventually, a point is reached where a particular clean up technology may no longer be a viable option. Here are some general examples of how crude oil properties impact spill response.

#### **3.1 Dispersants**

During a real oil spill, dispersant effectiveness is largely weather dependent and can be affected by ambient conditions of the surrounding environment such as temperature or water salinity. For example, dispersants typically work better in saline water, and are less efficient in lower salinities. However, oil viscosity may be used to roughly indicate how effective dispersant application will be. According to the CNA report, *Oil Properties and Their Impact on Spill Response Options*, dispersants become less effective as weathering occurs and oil increases in viscosity (5, p.25). Through conducting a literature review of dispersant studies, CNA found ranges of dispersant effectiveness based on different ranges of ANS viscosity. Table 3, taken from the CNA report, shows how dispersants are no longer a viable response option for ANS once viscosity exceeds 10,000 cP.

### **3.2 In-Situ Burning**

In-Situ Burning involves igniting an oil spill in place in order to remove it from water through burning. How easily an oil spill is ignited may depend on several things including how readily it vaporizes or how much water content it has. In general, lighter oils ignite more readily than heavier oils due to increased evaporation of lighter hydrocarbons. The CNA report identifies API gravity as being the single biggest predictor of ignitability (5, p.18). CNA again determined ranges of API gravity for in-situ burning effectiveness by conducting a literature review of various testing reports. Table 4 indicates API gravity boundaries for burning based on the CNA report. Heavy oils with an API gravity of 20 or less are no longer ignitable (5, p.18).

### **3.3 Mechanical Recovery**

Mechanical equipment may be used to physically separate oil from the underlying water column, thus removing it without using any chemicals or burning. Many different types of mechanical oil recovery equipment, called skimmers, are manufactured. For instance, weir skimmers allow floating oil to pass over a lip into the skimmer, and brush skimmers attract oil onto rotating brushes. Figure 3 shows which type of skimmers are useful with increasing oil viscosity. The American Society of Testing and Materials (ASTM) standard skimmer categories are given in Table 5. Typically weir skimmers are more effective in lower viscosity oils and brush or drum skimmers are more effective in weathered, high viscosity oil (5, p.41). Important to note is hybrid skimmers with new technologies, for instance disk skimmers with micro brush coatings on the disks, may be effective beyond the typical ranges shown in Figure 3.

## 4. Presentation of 2015 ANS Testing Results

The Prince William Sound Regional Citizen's Advisory Council (PWSRCAC) obtained a sample of ANS in 2015 and had it shipped to an Environment Canada lab for testing. Environment Canada is Canada's equivalent to the US Environmental Protection Agency or EPA. PWSRCAC had this testing done in parallel with industry tests performed by SL Ross Environmental Research Ltd in order to compare results. Both testing agencies reported very similar findings. A few of Environment Canada's testing results will now be discussed.

### 4.1 Viscosity

Figure 4 contains 2015 ANS viscosity testing results from Environment Canada. Test procedures allowed the ANS sample to evaporate under laboratory conditions in order to simulate weathering. Samples were tested at different evaporative mass losses to see how properties change with weathering. Figure 4 shows two separate curves, one at 0 degrees Celsius (32 °F) and one at 15 degrees Celsius (59 °F). Tests were done at different temperatures to simulate differences between summer and winter conditions. Viscosity is temperature dependent, and lower temperatures resulted in higher viscosity. Figure 4 is a representation of how viscosity increases over time with weathering. Table 3 indicates the effectiveness of dispersants is reduced to less than 70 percent once ANS viscosity exceeds 1000 cP. Using lines of best fit with Figure 4, this value could be reached after ANS is approximately 25.2 to 35.9 percent evaporated, depending on temperature.

## 4.2 Density

ANS density in 2015 is shown as API gravity in Figure 5. Two different curves are again shown for two different temperatures. A high API gravity corresponds to a light crude oil. At time zero, ANS is a light oil. As evaporation occurs, ANS becomes heavier due to removal of light molecular-weight compounds. Density is also temperature dependent and increases with colder temperatures due to thermal contraction of materials. Table 4 indicates how easily crude oil may be ignited using API gravity, as a general rule of thumb. Once oil has weathered to the point where API gravity falls to 20 or less, in-situ burning may no longer be usable. Using lines of best fit with Figure 5, this point may be reached once ANS has evaporated approximately 25.9 to 30.9 percent, depending on temperature. Both Figures 4 and 5 indicate cold temperatures are worse for oil spill cleanup efforts. For example, at colder temperature, ANS would only have to evaporate 25.9% before in-situ burning becomes unusable, versus 30.9% evaporative loss for warm temperature.

## 4.3 Emulsion Formation Tendency

Results presented so far have indicated how viscosity and density change with evaporation. ANS samples were also tested for emulsion formation tendency at various stages of evaporation. Those results are summarized in Table 6. Based on Environment Canada's observations, ANS is not likely to form an emulsion until it has undergone extensive evaporation over a long time period. The resulting emulsion which formed had relatively low water content, approximately 20 percent water by weight.

Emulsion formation tendency and ability are greatly affected by asphaltene and resin contents. Figure 6 shows SARA content of 2015 ANS at four stages of evaporation. Asphaltene and Resin contents steadily increase with weathering, however, these compositions apparently were not enough to cause ANS to form a stable emulsion.

#### **4.4 Change in ANS Properties Over Time**

Test data over a 10 year span indicate little change in ANS properties. Figure 7 shows ANS density over an approximate 10 year span, from 2004 to 2015. Testing results have been nearly identical during this time frame. This trend indicates there are no expected changes in ANS properties, at least not in the near future.

Looking back over a longer time frame, ANS properties have changed. Figure 8 shows ANS testing for density, with results going back to 1983 (3, p.7). Since Exxon Valdez, ANS has gotten lighter because lighter, more valuable oil fields have been developed on the North Slope. As previously mentioned, mousse emulsion was encountered during the Exxon Valdez spill. This is because ANS had different properties in 1989 - it was much denser than it is today. If ANS density increased in the future, the tendency of ANS to form an emulsion could also be increased depending on chemical composition. This could happen for instance if oil companies produced different oil fields on the slope.

#### **4.5 Weathering Rates**

Laboratory results have so far indicated evaporation will have the most significant effects on ANS crude's properties, since ANS is unlikely to emulsify. Figure 9 shows laboratory

results for evaporative testing of ANS (6, p.5). This data was obtained by allowing the sample to evaporate under controlled conditions, and then taking sample weights periodically to see how much was lost to evaporation. A logarithmic equation was fitted to the data in order to calculate a precise time for any stage of evaporation. Table 7 shows calculated times based on this equation to reach each of the 3 evaporative percent losses used in testing. These are approximately one third and two thirds of total evaporation of 36%. Table 7 shows the first third is gone within 40 minutes, the second third takes an additional 24 hours, and to get the last third to evaporate takes an additional 30-some days. These results are consistent with general evaporation trends of petroleum (Figure 2).

## **5. Window of Opportunity for Spill Response**

Laboratory testing allows us to predict ANS crude properties at various stages of weathering, and determine approximately how long it would take for those changes to occur. Windows of opportunity for each spill response method may be defined using testing results as guidelines. Examples of such timeframes are shown in Figure 10 for three major recovery techniques. Actual windows of opportunity will vary depending on weather and ambient environmental conditions; these guidelines are merely to be taken as general rules of thumb. Colder temperatures may shorten the windows of opportunity for in-situ burning and dispersants. The CNA report estimates light crude oils may remain burnable for 40 to 60 hours after a spill, therefore estimated timeframe for using in-situ burning is approximately 2 days (5, p. 19). The timeframe for using dispersants was determined based on how long it would take to reach 30% evaporative loss, which is roughly the midpoint between warm and cold

temperature results for 1000 cP viscosity (Figure 4). Using the equation from Figure 9 to solve for time  $t$ , this would take approximately 5 days. Therefore, the initial 5 days after an oil spill is an estimated timeframe for when dispersants will be most effective. Mechanical recovery encountered no hold-ups at either temperature range. Based on Tables 8 and 9, ANS oil falls within ASTM categories I, II, and II - III depending on weathering and temperature. Prince William Sound has a variety of skimming equipment suitable for effective response in those category ranges. Therefore, mechanical recovery has no discernable time limit. While testing results indicate ANS is unlikely to emulsify, it is worth noting that high sea energy could cause water uptake. This would adversely affect mechanical recovery - for instance having to deal with higher volumes of fluid.

## **6. Conclusions and Summary**

Testing results requested by PWSRCAC indicate no major changes in 2015 for ANS crude oil properties from prior testing done in 2013. Trends indicate ANS properties such as viscosity and density are remaining relatively constant. However, ANS properties could change if different oil fields are produced on Alaska's North Slope or if reservoir depletion leads to changes in oil currently being produced.

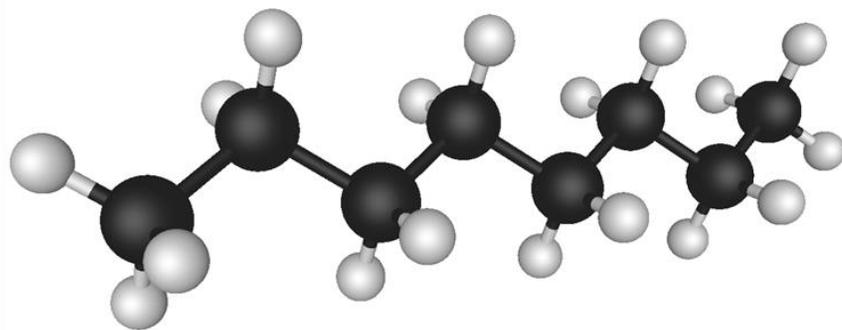
Laboratory testing of ANS provides hard scientific data for determining the appropriateness of oil spill response methods. Based on 2015 testing results, Prince William Sound would have appropriate response options in place during the event of an oil spill. Cold temperatures could shorten the window of opportunity for using response options like dispersants and in-situ burning. However, mechanical recovery, the primary cleanup

technology for Prince William Sound, would likely remain effective over a wide range of temperatures and oil properties. Actual windows of opportunity for spill response will vary depending on ambient environmental conditions.

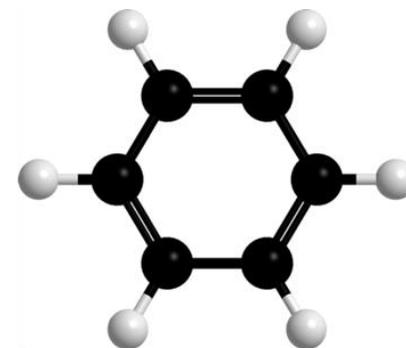
## 7. References

- [1] *Oil in the Sea III: Inputs, Fates, and Effects*. National Research Council, The National Academies Press, 2003
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- [3] Spill Related Properties of ANS Crude in 2015, SL Ross Environmental Research Ltd., June 2015
- [4] Fingas Merv, *Analytical Data on Crude Oils Necessary for Oil Spill Work*, June 2008
- [5] Federici, Mintz, *Oil Properties and Their Impact on Spill Response Options; Literature Review*, CNA Analysis & Solutions, May 2014
- [6] Hollebhone, Bruce, *Physical Properties, Behavior and Composition of Alaskan North Slope Crude Oil*, Environment Canada, Ottawa, February 2016
- [7] *Responding to Oil Spills in the U.S. Arctic Marine Environment*. National Research Council, the National Academies Press, 2014 (NRC, 2014)
- [8] *Marine Pollution*, 5<sup>th</sup> edition, Clark, R.B., Oxford University Press, 2001 (Clark, 2001)

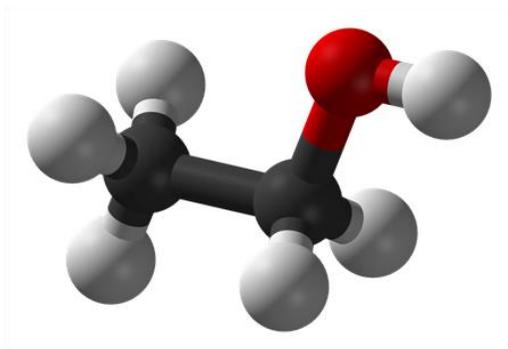
## **Appendix A: Figures**



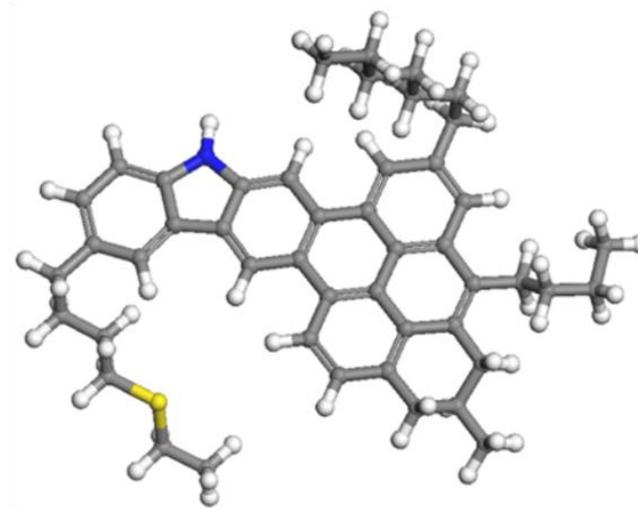
Saturate (octane)



Aromatic (benzene)

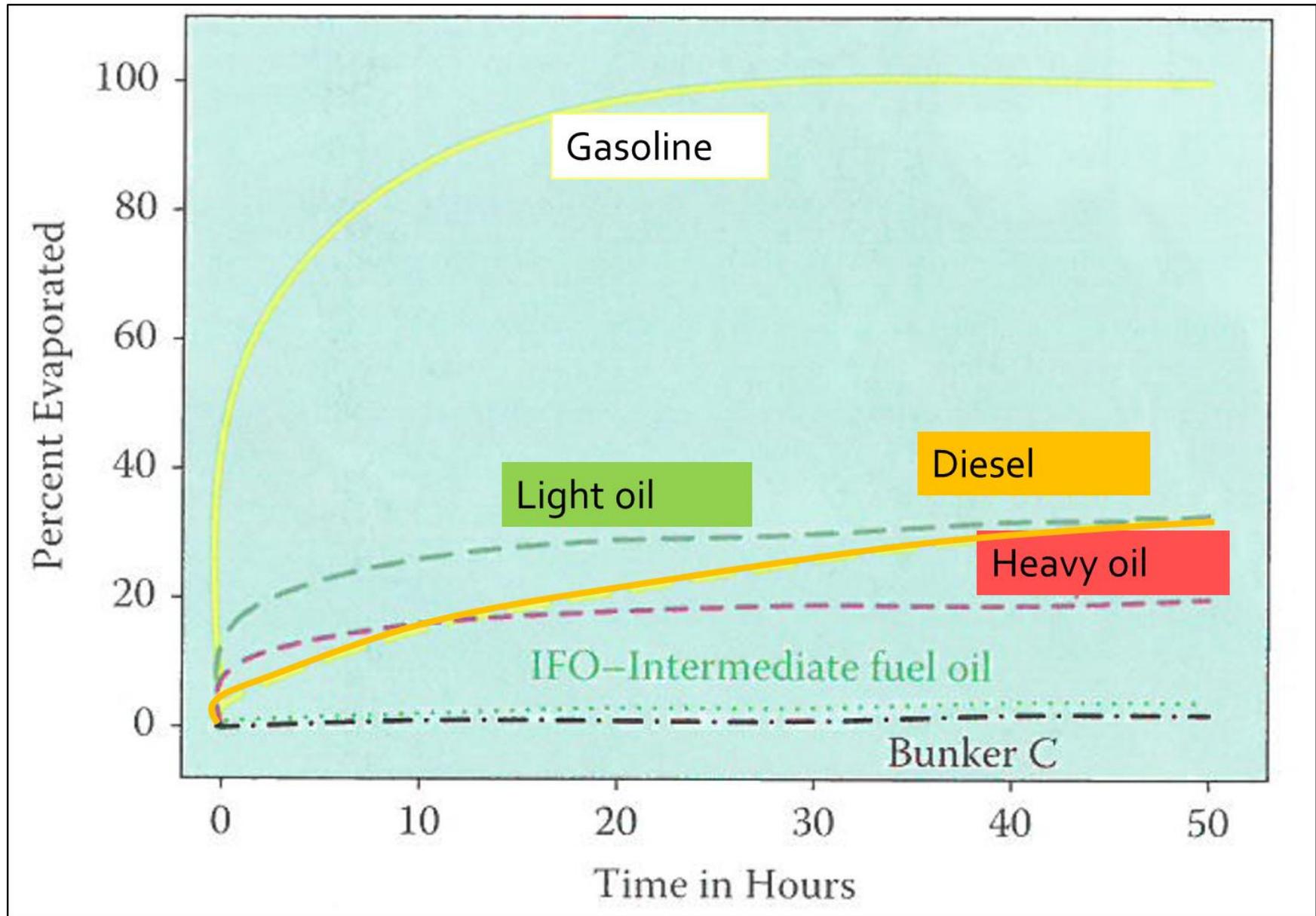


Resin (ethanol)

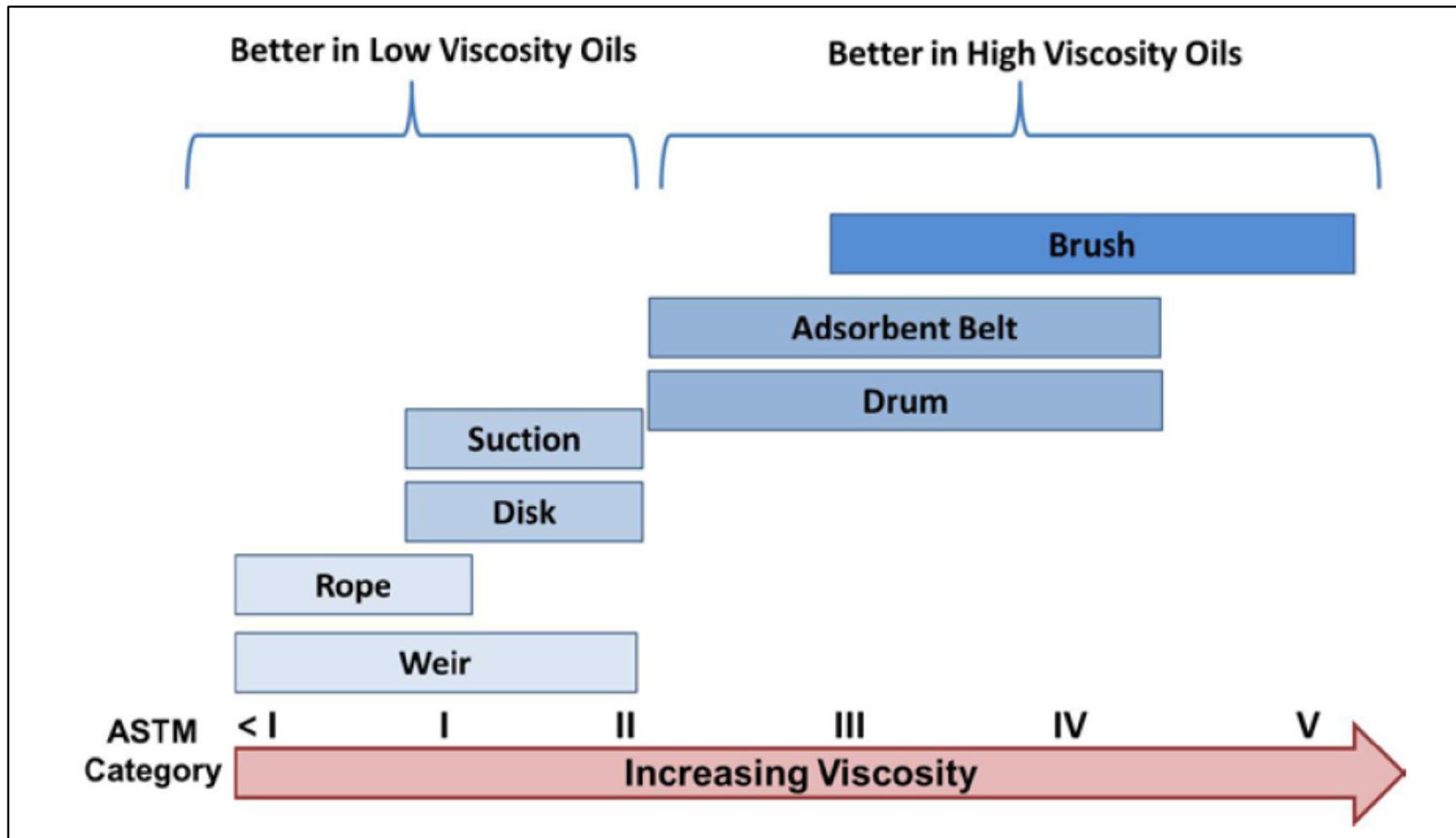


Asphaltene

**Figure 1:** Examples of molecules found within crude oil. Each molecule represents a different chemical category.

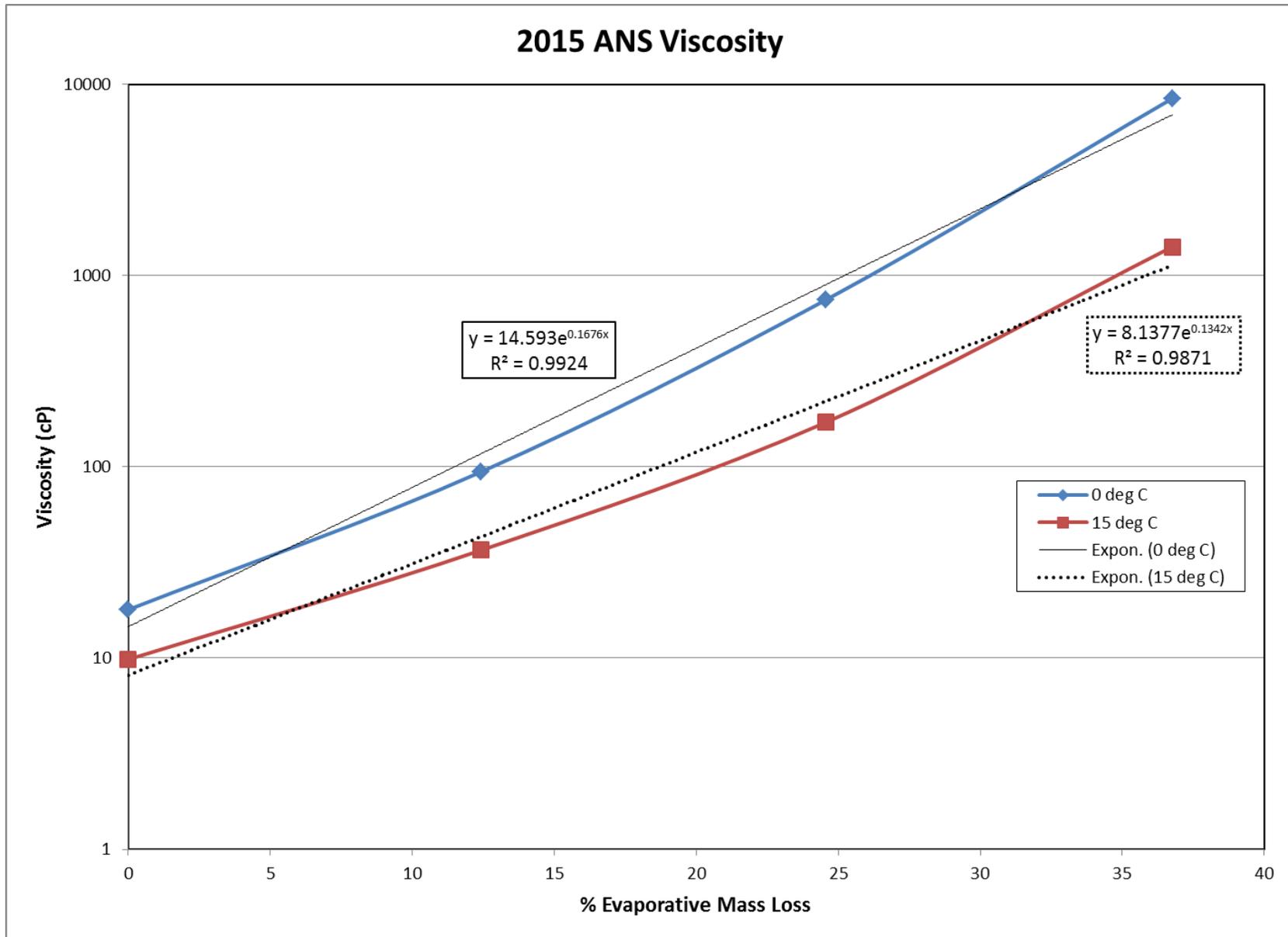


**Figure 2:** Evaporation curves of various petroleum products. (adapted from *The Basics of Oil Spill Cleanup*, Merv Fingas, 2013)

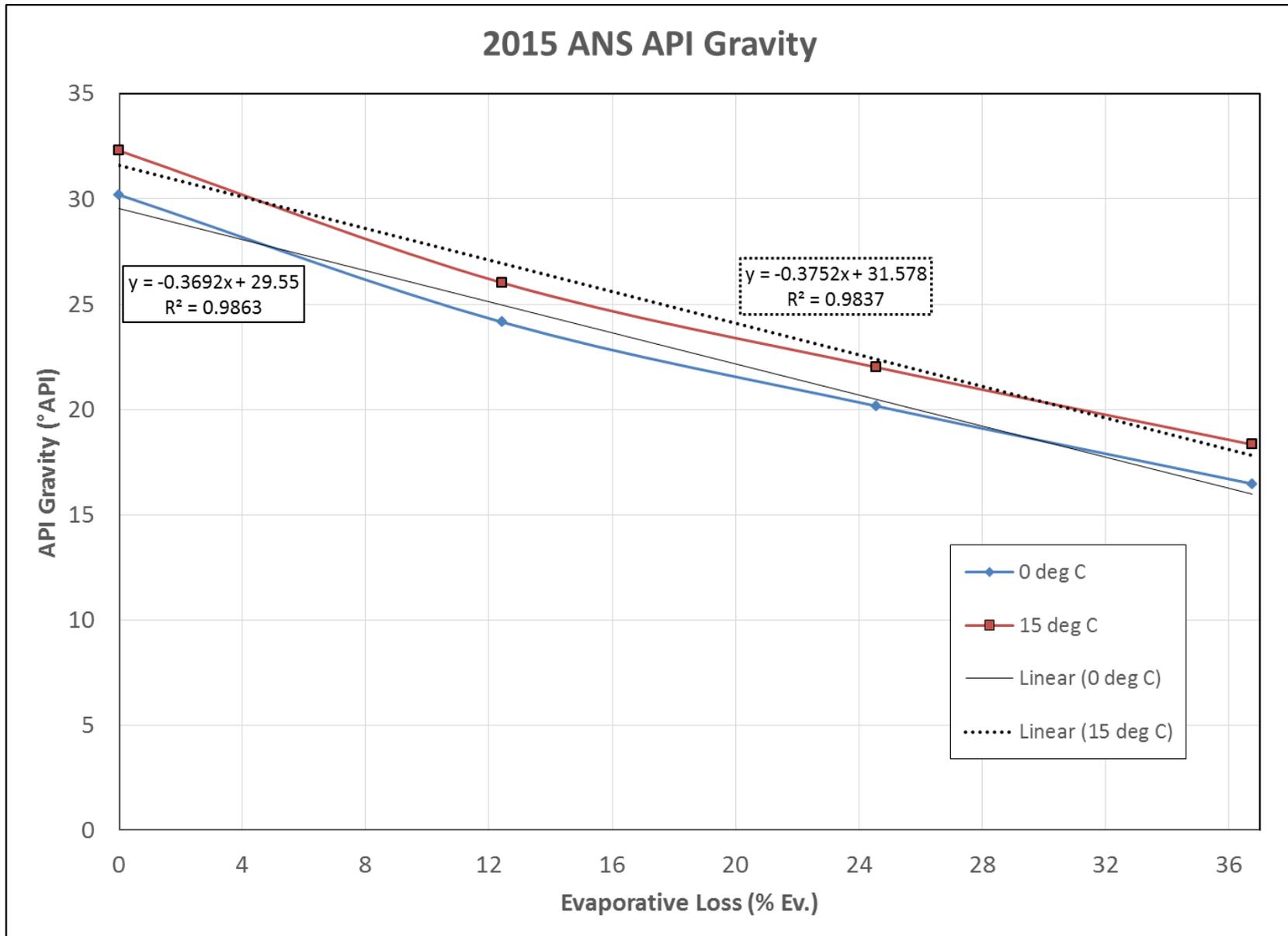


**Figure 3:** Effectiveness of different skimmer types with increasing viscosity. (from *Oil Properties and Their Impact on Spill*

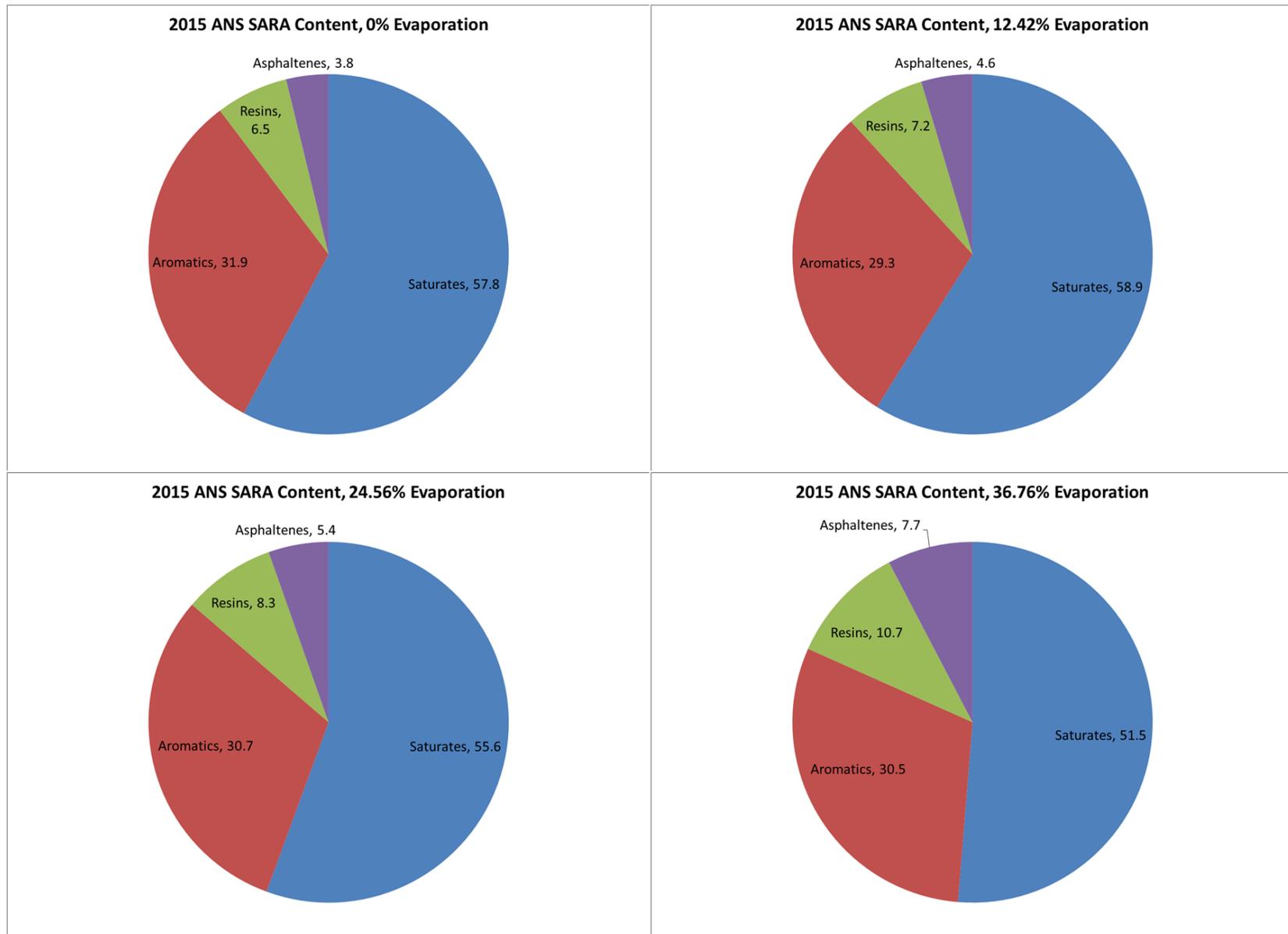
*Response Options*, Carolyne Federici, Jonathon Mintz, 2014)



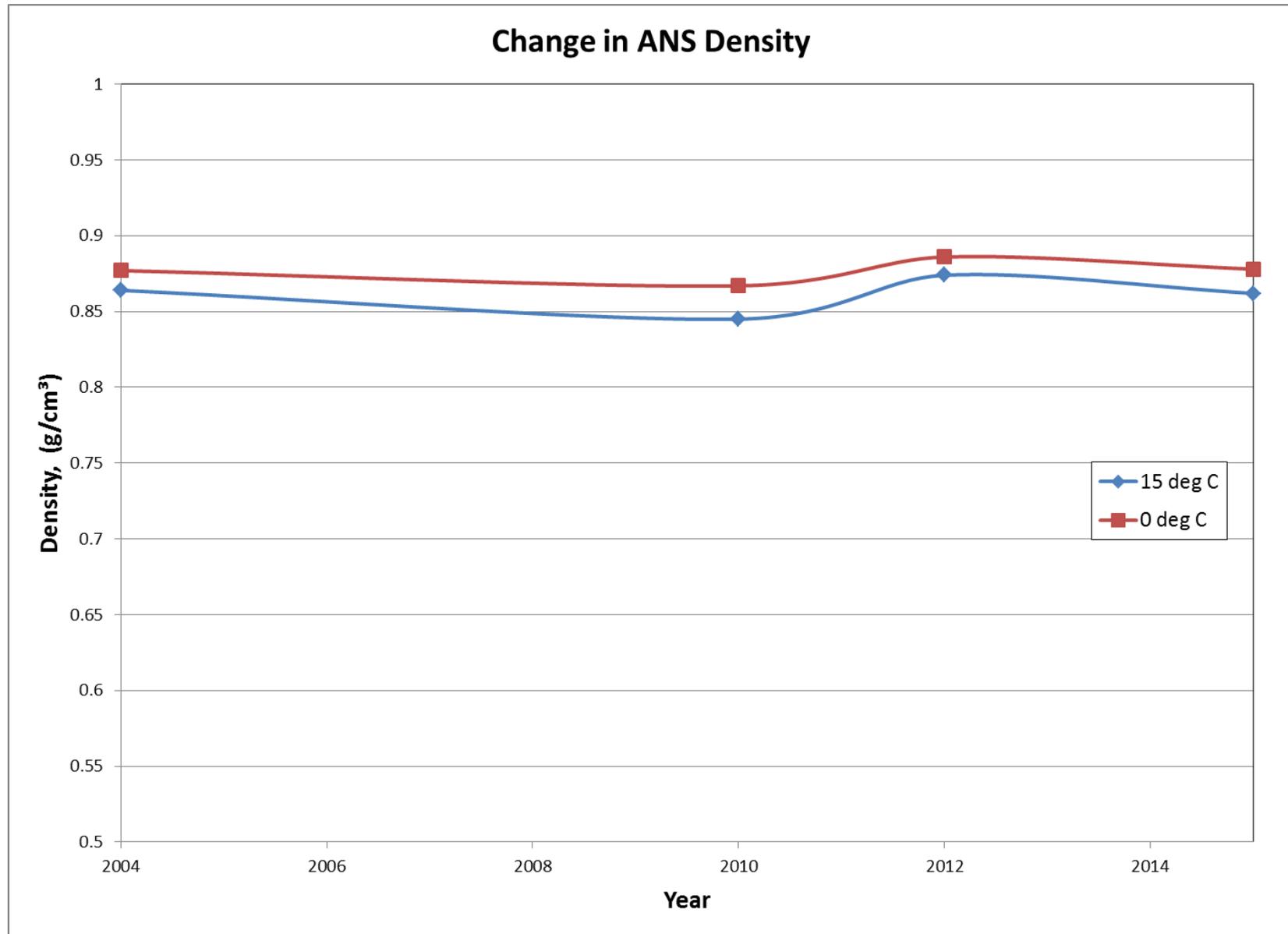
**Figure 4:** Graph of ANS viscosity as a result of weathering, 2015. (source: Environment Canada)



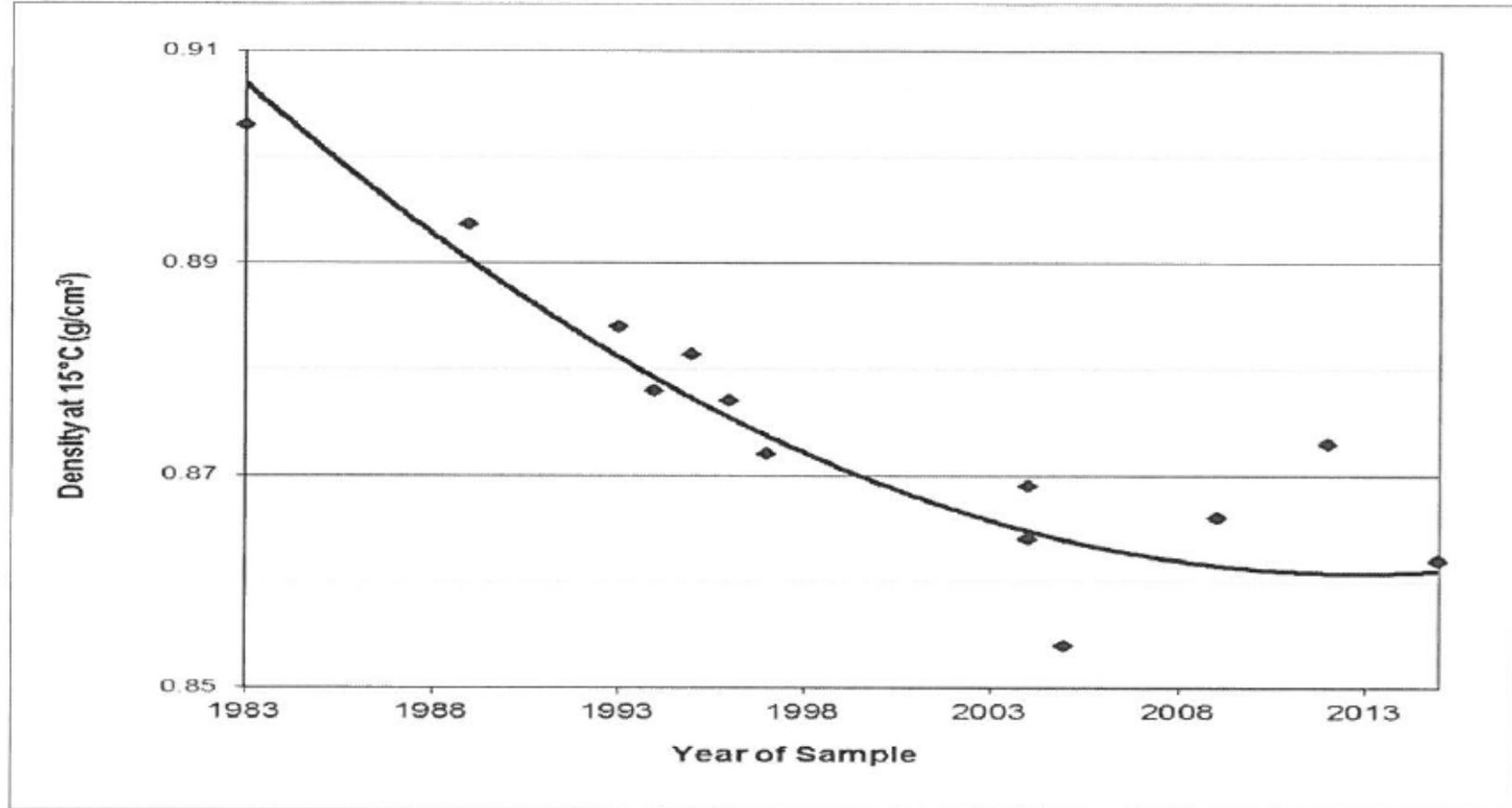
**Figure 5:** Graph of ANS API gravity as a result of weathering, 2015. (source: Environment Canada)



**Figure 6:** SARA content of ANS as a result of weathering, 2015. (source: Environment Canada)

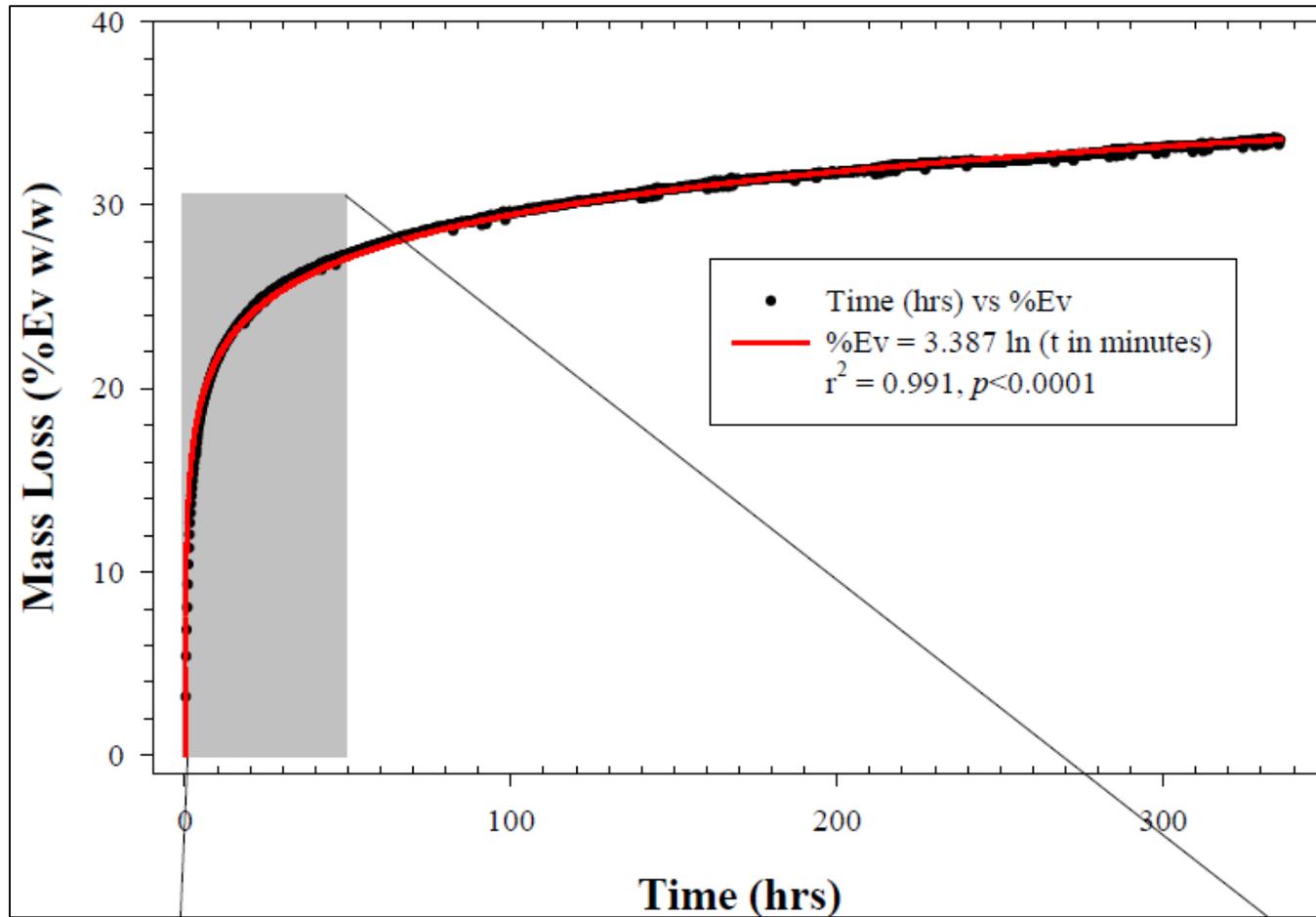


**Figure 7:** ANS crude oil properties over a 10 year span. (source: Environment Canada)

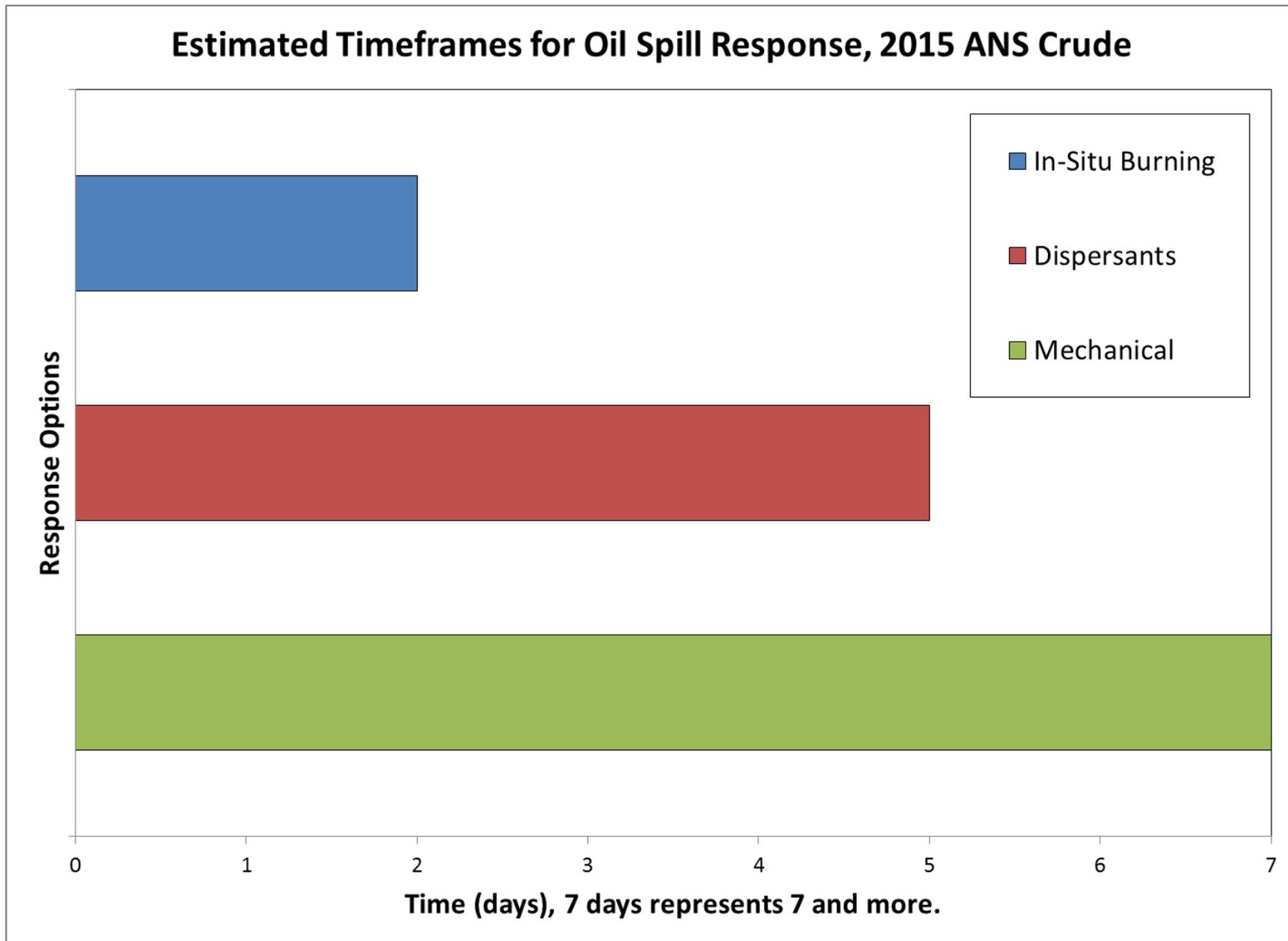


### Change in Fresh ANS Density Over time

**Figure 8:** ANS crude oil properties over a 30 year span. (From *Spill Related Properties of ANS Crude in 2015*, SL Ross, June 2015)



**Figure 9:** Evaporation Curve of ANS, 2015. (from *Physical Properties, Behaviour, and Composition of Alaskan North Slope Crude Oil*, Environment Canada, February 2016)



**Figure 10:** Using laboratory testing results to determine windows of opportunity for oil spill response options. (source:

Environment Canada)

## **Appendix B: Tables**

<b>Fluid</b>	<b>°API</b>
light oil	> 31.1
medium oil	31.1-22.3
heavy oil	<22.3
(fresh water)	10

<b>Type</b>	<b>Water Uptake (%)</b>
unstable	-
entrained	30 - 40
mesostable	50 - 70
stable	60 - 80

<b>Table 3: Dispersability of ANS</b>		
<b>Category</b>	<b>Viscosity (cP)</b>	<b>Effectiveness (%)</b>
dispersable	< 1,000	> 70
reduced dispersability	1,000 - 10,000	70 - 5
not dispersable	> 10,000	< 5

Source: *Oil Properties and Their Impact on Spill Response Options*, CNA 2014

<b>Table 4: In-Situ Burning</b>	
<b>Category</b>	<b>°API</b>
easy to burn	> 35
burnable, variable ignitability	35 - 20
unignitable	< 20

Source: *Oil Properties and Their Impact on Spill Response Options*, CNA 2014

**Table 5: ASTM Skimmer Categories**

Category	Viscosity (cSt)	Density (g/mL)
I	150 – 250	0.90 – 0.93
II	1,500 – 2,500	0.92 – 0.95
III	17,000 – 23,000	0.95 – 0.98
IV	50,000 – 70,000	0.96 – 0.99
V	130,000 – 170,000	0.96 – 0.99

Source: *Oil Properties and Their Impact on Spill Response Options*, CNA 2014

**Table 6: 2015 ANS Emulsion Tendency & Stability**

% Evaporative Mass Loss	Emulsion Stability	Water Content	Viscosity (cP)
0.00	Unstable	0.04	66
12.42	Unstable	0.20	100
24.56	Unstable	1.03	200
36.76	Meso-Stable	22.80	2400

<b>Table 7: Weathering Time for 2015 ANS</b>				
<b>Mass Loss (% Ev.)</b>	0.00	12.42	24.56	36.76
<b>Time</b>	-	39.1 minutes	23.5 hrs	35.9 days

<b>Table 8: 2015 ANS Properties, 0° C</b>			
<b>Mass Loss (% Ev)</b>	<b>Density (g/mL)</b>	<b>Kinematic Viscosity (cSt)</b>	<b>ASTM Skimmer Category</b>
0.00	0.88	20	< I
12.42	0.91	104	I
24.56	0.93	799	I - II
36.76	0.96	8812	II - III

<b>Table 9: 2015 ANS Properties, 15° C</b>			
<b>Mass Loss (% Ev)</b>	<b>Density (g/mL)</b>	<b>Kinematic Viscosity (cSt)</b>	<b>ASTM Skimmer Category</b>
0.00	0.86	10	< I
12.42	0.90	41	< I
24.56	0.92	185	I
36.76	0.94	1496	II