

2 Oil Behavior and Toxicity

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Chapter 2.

Oil Behavior and Toxicity

Composition of Crude Oils

Crude oils are complex mixtures which vary widely in composition. However, they can be divided into three broad groups of compounds which help the responder assess the initial impacts and fate of the oil. These groups are very simple:

- 1) Light-weight components
- 2) Medium-weight components
- 3) Heavy-weight components

We use compositional data on crude oils to characterize them as to the amounts of each group present in the oil, and thus predict the behavior of the oil and the risk the oil poses to natural resources of concern.

Light-weight components are characterized by:

- Hydrocarbon compounds containing up to ten carbon atoms
- A boiling range up to 150 degrees C
- Rapid and complete evaporation, usually within a day
- High water solubility; usually contributes >95% of water-soluble fraction
- High acute toxicity because they contain the monoaromatic hydrocarbons (benzene, toluene, xylene) which are soluble and toxic
- No potential for bioaccumulation (they evaporate instead)
- Mostly composed of alkanes and cycloalkanes which have relatively low solubility (and thus low acute toxicity potential)

These light ends evaporate so quickly that they do not persist in the environment. Even though individual aromatic compounds have solubilities of over 1,000 mg/L, they are rapidly removed from solution by evaporation. One important exception to this general rule is when the dissolved fraction is rapidly mixed into the water column under cold conditions, as occurred during the Ashland spill of over 1

million gallons of No. 2 fuel oil into the Monongahela River on 2 January 1988. To make conditions even worse, the spill flowed over numerous locks and dams, which caused the oil to mix throughout the water column as it plunged over the dams. Dissolved and dispersed oil was detected in the river for hundreds of miles downstream.

Medium-weight components are characterized by:

- Hydrocarbon compounds containing between 10 and 22 carbon atoms
- A boiling range from about 150 to 400 degrees C
- Evaporation rates of up to several days, although there will be some residue which does not evaporate at ambient temperatures
- Low water-soluble fraction (at most a few mg/L)
- Moderate acute toxicity because they contain diaromatic hydrocarbons (naphthalenes) which are toxic in spite of their low solubilities
- Moderate potential for bioaccumulation and chronic toxicities associated with the diaromatic hydrocarbons
- Alkanes which are readily degraded

These medium-weight components pose the greatest environmental risks to organisms because the compounds are more persistent, they are biologically available, and the PAHs have high toxicities. The alkanes (aliphatic hydrocarbons) are readily biodegraded under the right conditions. In fact, chemists monitor the distribution of these compounds over time to show the process of degradation of a spill.

The heavy-weight components are characterized by:

- Hydrocarbon compounds containing more than 20 carbon atoms
- Almost no loss by evaporation
- Almost no water-soluble fraction

- Potential for bioaccumulation, via sorption onto sediments, otherwise not highly bioavailable
- Potential for chronic toxicity, because they contain polynuclear aromatic hydrocarbons (phenanthrene, anthracene, etc.)
- Most of the components are waxes, asphaltenes, and polar compounds which do not have any significant bioavailabilites or toxicities
- Long-term persistence in sediments, as tar balls, or asphalt pavements

These heavier components pose little acute toxicity risks, except that due to smothering, because of the very low solubilities of the individual compounds. Animals have to be exposed via a sediment pathway or through the food chain. However, these are the most persistent components of an oil, and degradation rates will be very slow.

Refined petroleum products, in contrast to crude oil, have only a very narrow range of components, and they are characterized according to boiling range fractions.

Weathering Processes at Oil Spills as Applied to Resources at Risk, Oil Persistence, and Cleanup

Evaporation

Evaporation is the single most important weathering process in the first several days of an oil spill (Fig. 2-1). For light, refined products such as gasoline, evaporation will remove 100 percent of the spill within a very short time. For heavy refined products such as No. 6 fuel oil or Bunker C, evaporation will only remove 5-10 percent of the spill. For crude oils, the amount of the spill lost to evaporation can range from 20 to 60 percent. For spills of medium crude oils, a rule of thumb is that 20-30 percent of the oil is lost to evaporation within the first 24 hours!

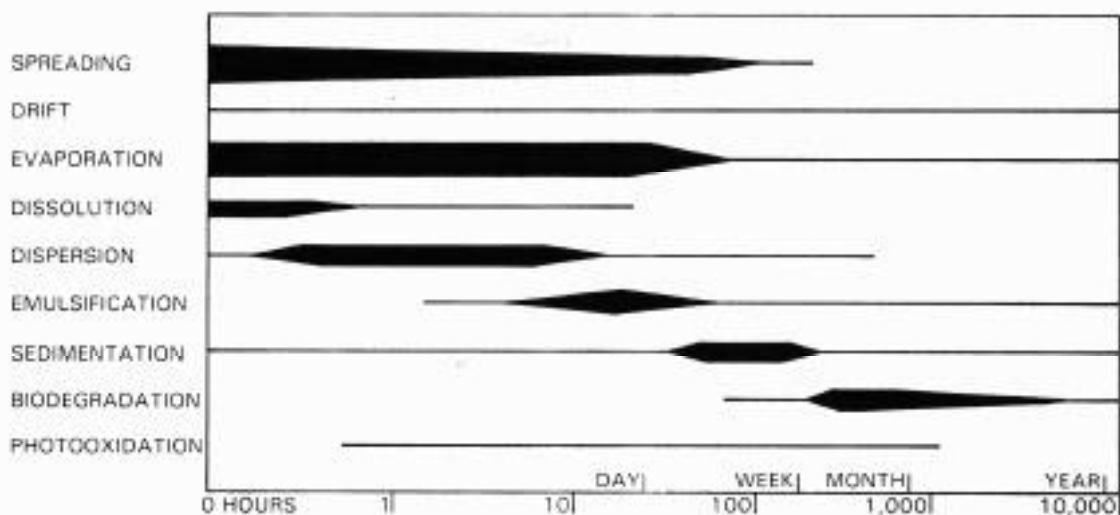


Figure 2-1. Schematic showing the relative importance of weathering processes of an oil slick over time. The width of the line shows the relative magnitude of the process in relation to other contemporary processes.

Payne et al. (1983) have developed an oil-weathering model which has a good evaporation sub-model in it. It uses the true boiling point distillation temperatures and the volume percent of the oil for each of these boiling point ranges, information which is usually available from the owner or shipper. This model is available for use on microcomputers, and it is relatively easy to use. The differences in the rate of evaporation for various oils can be shown by running the model for two different spills: the *Exxon Valdez* spill of Prudhoe Bay crude, a medium-heavy oil, spilled under cold conditions (March 1989), where 10 percent was calculated to have evaporated within the first 24 hours; and the *Mega Borg* spill of Angola crude, a light oil, spilled in June 1990, where 45 percent was calculated to have evaporated within the first 24 hours.

Environmental factors which affect the rate of evaporation are:

- Area of slick exposed, which changes rapidly
- Wind speed and water surface roughness
- Air temperature and solar radiation
- Formation of emulsions, which dramatically slows evaporation

Windy, sunny days and currents which rapidly spread the slicks speed evaporation. Evaporation even removes dissolved hydrocarbons from the water column. Figure 2-2 shows the concentration of the volatile aromatic hydrocarbons in the water-soluble fraction of Prudhoe Bay crude over time as measured in laboratory tests. These compounds are lost via evaporation from the water.

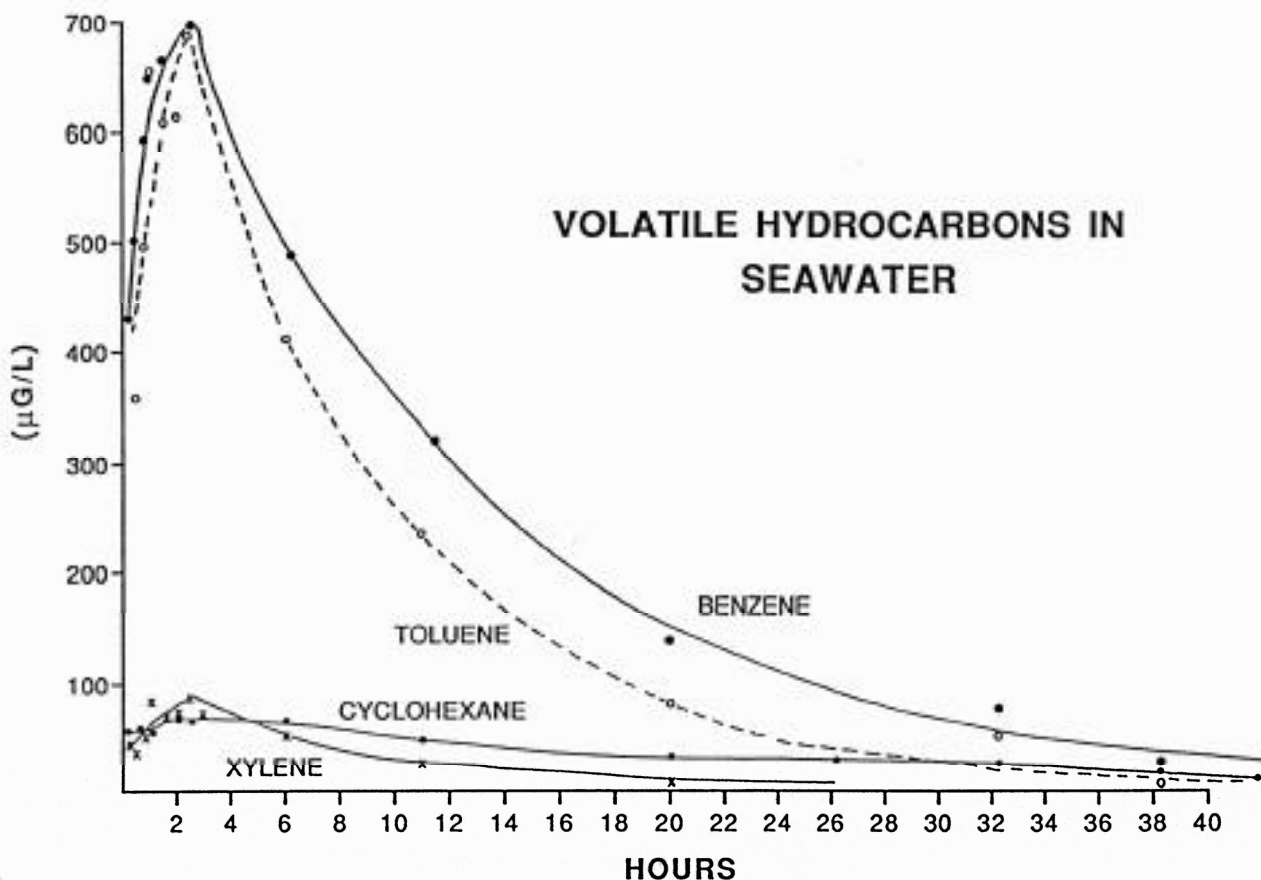


Figure 2-2. Plot of the concentrations of volatile aromatic hydrocarbons in the water-soluble fraction of Prudhoe Bay crude oil over time. Note the rapid loss of these compounds by evaporation (Payne et al., 1983).

Dissolution

Dissolution of petroleum hydrocarbons into the water column poses risks to aquatic organisms because of the acute toxicity of the compounds that have significant water solubility. Figure 2-3 shows the solubility of normal alkanes, cycloalkanes, and aromatic hydrocarbons in fresh water. It should be noted that solubilities in sea water are lower, by about 70 percent (Sutton and Calder, 1974). Compounds with

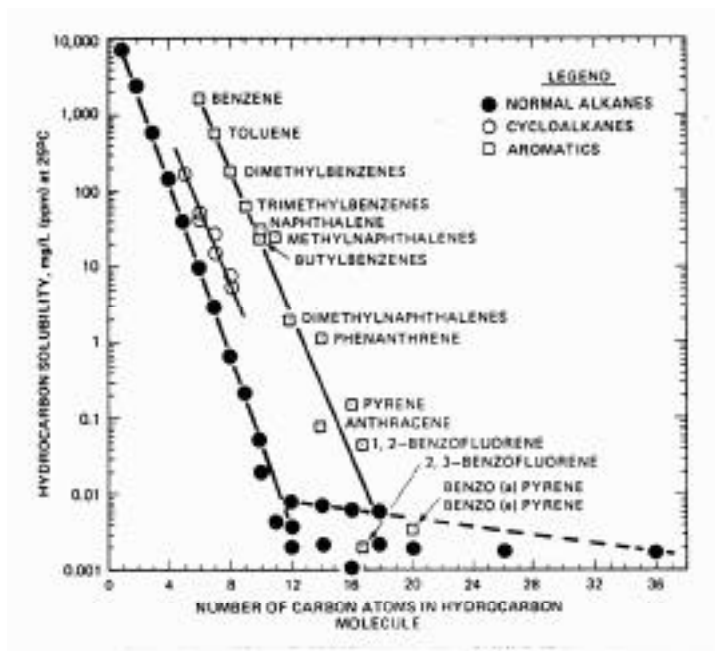


Figure 2-3. Water solubility of the major components of crude oil, for three groups of compounds, plotted by carbon number. (McAuliffe, 1983)

carbon numbers less than four are gases at ambient temperatures, so they are not of concern. The monoaromatics have the highest solubilities, by a factor of 50, than similar weight alkanes. Benzene has the highest solubility, at 1,750 mg/L, with toluene at 515 mg/L, and xylene less than 100 mg/L. McAuliffe (1987) reported the water-soluble fraction of six oils equilibrated with saline water, ranging from 20 to 40 ppm total dissolved hydrocarbons. Benzene plus toluene constituted from 70-85 percent of the aromatic fraction, and total aromatics constituted 35-80 percent of the total dissolved hydrocarbons. Of the higher PAHs, naphthalene is the most water-soluble, contributing 0.12 ppm to the water-soluble fraction of south Louisiana crude and 0.02 ppm for Kuwait crude (McAuliffe, 1987). The amount of the next heavier PAHs in the water-soluble fraction is 100 times lower than the naphthalenes.

Emulsification

Formation of emulsions affects the behavior of an oil spill in many ways. First, weathering rates are much slower. The oil is more viscous and sticky. The volume of "oil" is increased by a factor of 2-3, because the emulsion is up to 70 percent water. Most recovery equipment works very poorly on mousse. Tendency to emulsify and emulsion stability is very closely related to the asphaltene content. Predicting the

formation and stability of emulsion is important. Based on laboratory and field experience, stable emulsions are likely to form for:

- Heavy crudes with high viscosities
- Crudes and refined products with high asphaltene content
- Crudes with high NSO compound content

Emulsification almost never occurs during spills of:

- Gasoline
- Kerosene
- Diesel fuels (except under VERY cold conditions)

General Spill Types and Behaviors

Based on all the properties of spilled oil, there are four types of oil for which a general assessment of the behavior and fate can be made:

Type 1—Very Light Oils (Jet Fuels, Gasoline)

- Highly volatile (should all evaporate within 1-2 days).
- High concentrations of toxic (soluble) compounds.
- Result: Localized, severe impacts to water column and intertidal resources.
- Duration of impact is a function of the resource recovery rate.
- No dispersion necessary.
- No cleanup necessary.

Type 2—Light Oils (Diesel, No. 2 Fuel Oil, Light Crudes)

- Moderately volatile; will leave residue (up to one-third of spill amount) after a few days.
- Moderate concentrations of toxic (soluble) compounds, especially distilled products.
- Will "oil" intertidal resources with long-term contamination potential.

- Has potential for subtidal impacts (dissolution, mixing, sorption onto suspended sediments).
- No dispersion necessary.
- Cleanup can be very effective.

Type 3—Medium Oils (Most Crude Oils)

- About one-third will evaporate within 24 hours.
- Maximum water-soluble fraction 10-100 ppm.
- Oil contamination of intertidal areas can be severe and long-term.
- Oil impacts to waterfowl and fur-bearing mammals can be severe.
- Chemical dispersion is an option within 1-2 days.
- Cleanup most effective if conducted quickly.

Type 4—Heavy Oils (Heavy Crude Oils, No. 6 Fuel Oil, Bunker C)

- Heavy oils with little or no evaporation or dissolution.
- Water-soluble fraction is less than 10 ppm.
- Heavy contamination of intertidal areas likely.
- Severe impacts to waterfowl and fur-bearing mammals (coating and ingestion).
- Long-term contamination of sediments possible.
- Weathers very slowly.
- Chemical dispersion seldom effective.
- Shoreline cleanup difficult under all conditions.

References

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