

PROPERTIES AND EFFECTS OF NONPETROLEUM OILS

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ABSTRACT

Legislative history of water pollution control has not included detailed scientific definitions of what is meant by the rather inclusive term "oil." Because of the publicity surrounding spills of crude or petroleum-derived oils, little attention has been focused on non-petroleum oils. Approximately 5% of the oil spills reported to the Environmental Protection Agency are nonpetroleum oils. Their physical and chemical properties and adverse environmental effects are strikingly similar to the behavior of petroleum oil in the aquatic environment. This paper presents a comparative analysis of the properties and effects of petroleum versus nonpetroleum oils. Their similarities prove that these oils should be treated as one entity regardless of their origin. Finally, additional guidelines are presented to provide a more broadly applicable distinction between oil and other hazardous materials for enforcement purposes.

INTRODUCTION

Section 311 of the Federal Water Pollution Control Act amendments defines oil as "oil of any kind or in any form including, but not limited to petroleum, fuel oil, sludge, oil refuse, and oil mixed with wastes other than dredged spoil." Unfortunately, legislative history of water pollution control has not included detailed scientific definitions of what is meant by the rather broad term "oil." The Environmental Protection Agency has interpreted the definition of oil to apply to nonpetroleum as well as petroleum oil.

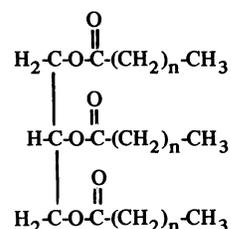
Petroleum oils are mineral or hydrocarbon oils produced from crude petroleum, while nonpetroleum oils consist of fatty oils derived from vegetable or animal fats and essential oils derived from plants. Because the fatty oils are produced in larger quantities and have a higher spill incidence than essential oils, this paper focuses on the harmful effects of discharges of vegetable oils and animal fats. Approximately 5% of the oil spills officially reported to the Environmental Protection Agency by a variety of producing and handling companies are nonpetroleum oils. Their physical and chemical properties and adverse environmental effects are strikingly similar to those of petroleum oils.

The objective of this paper is to compare the effects of petroleum and nonpetroleum oils in the aquatic environment. Case histories are described to underscore the similarities, and guidelines are presented for distinguishing all kinds of oil from other hazardous materials where the previous rationale fails to provide a clear distinction.

Physical and chemical properties

Vegetable oils and animal fats are water-insoluble substances which consist predominantly of glyceryl esters of fatty acids, or triglycerides [1]. Triglycerides contain approximately 95% fatty

acids and 5% glycerol combined as esters, with the following general structure:



They serve as an important source of free fatty acids which are released by caustic hydrolysis of the ester bonds. Because the fatty acid radicals constitute the greater part of the glyceride molecule, the chemical and physical properties of vegetable oils and animal fats are determined largely by the properties of its component fatty acids.

Fatty acids are defined as carboxylic acids derived from or contained in animal fats or vegetable oils. All fatty acids are composed of a saturated or unsaturated hydrocarbon chain of alkyl groups, containing from 4 to 22 carbon atoms and characterized by a terminal carboxyl group [2]. Fatty acids in vegetable oils are mostly 16 and 18 carbons in length, while in animal fats 20 and 22 carbon chains are found as well.

Petroleum and most high-volume petroleum products are extremely complex mixtures of chemical compounds. Many classes of compounds are present in petroleum, and each class is represented by many components. For example, hydrocarbons are a major class of constituents of petroleum. The hydrocarbons include the subclasses normal, branched, cyclic, saturated, and aromatic hydrocarbons. The subclass of normal hydrocarbons is represented by 10 to 60 individual members in many petroleum oils and products [3].

Similar behavior of fatty acids and petroleum oil in the aquatic environment is largely a result of their predominantly hydrocarbon character. Because of common physical and chemical properties, a parallel can be drawn between animal fats and oils, vegetable oils, fatty acids, and petroleum oils. Properties attributed to the long-chain hydrocarbons present in all fats and oils are summarized below:

1. limited water solubility and high solubility in organic solvent,
2. formation of surface slicks, and
3. ability to form emulsions and sludges.

Because animal fats and vegetable oils share similar physical and chemical properties with petroleum oil, the Environmental Protection Agency considers them a potential danger to the aquatic environment.

Other evidence supporting the similarity of nonpetroleum oils to petroleum oils is the use of the same analytical method to detect

and measure both substances. For purposes of water pollution control, this lends additional credence to the interpretation that these substances should be regulated in a similar manner. The oil-and-grease method approved by the Environmental Protection Agency in Guidelines Establishing Test Procedures for Analysis of Pollutants is the procedure described in *Standard Methods for the Examination of Water and Wastewater* [4,5]. It employs liquid-liquid extraction with trichlorotrifluoroethane as the extracting solvent. The method has found acceptance as the analytical parameter in water quality assessment such as the National Pollutant Discharge Elimination System (NPDES) permit program and effluent guideline limitations. The oil-and-grease procedure is the only method approved as standard, and it does not distinguish between petroleum and nonpetroleum oils.

Although standard analytical methods could be developed to differentiate between petroleum and animal or vegetable derived materials, no such development has been required to address the relevant water pollution aspects of the two contaminants. The physical and chemical properties and environmental effects of both types of materials are sufficiently similar to negate the need for differentiation.

Associated with the low solubility and density of nonpetroleum oils is their ability to form a layer on the surface of the water. This occurs because of the presence of the hydrophilic ester bonds, which dissolve in water, and the hydrophobic hydrocarbon chain which is water insoluble and therefore distributes itself on top of the water. This monomolecular layer covering the surface of the water produces a sheen. Although due to a different phenomenon, this property is common to petroleum oils as well and is used by the Environmental Protection Agency as a test to determine whether oil has been spilled in sufficient quantity to be harmful.

Environmental effects

The effects of nonpetroleum oils are similar to the effects of petroleum oils because of the physical properties common to both. Like petroleum oils, vegetable oils, animal fats, and mixed fatty acids may occur at four levels of the aquatic environment: (1) floating on the surface, (2) emulsified in the water column, (3) solubilized, and (4) settled on the bottom as a sludge. Associated with the ability to form surface films and slicks is the ability to form emulsions under proper environmental conditions. Conditions such as agitation by surf action, wind current, rapidly flowing streams, and prolonged exposure to heat from sunlight may lead to the formation of emulsions at the water-solid interface. When the emulsions and surface films or masses become engaged with debris, they can settle to the bottom as a sludge.

Oily substances of any kind may possibly be harmful to aquatic life and waterfowl in the following manner:

1. Free oil and emulsions may act on the epithelial surfaces of fish. If the concentration of oil is too heavy, oil will accumulate on the gills and prevent respiration. Oil and emulsions may coat and destroy algae and other plankton, thereby removing a source of fish food. The coated organisms may agglomerate with suspended solids and settle to the bottom.
2. Settled oily substances may coat the bottom, destroy benthic organisms, and interfere with spawning areas.
3. Soluble and emulsified material, ingested by fish, taint the flavor and may cause intestinal lesions due to laxative properties.
4. The biochemical oxygen demand (BOD) of organic materials may deoxygenate the waters sufficiently to kill fish. Heavy coatings of free oil on the surface may interfere with the natural processes of reaeration and photosynthesis.
5. Water-soluble constituents may exert a direct toxic action on fish or fish-food organisms [6].
6. Lethal effects on waterfowl may be drowning because of loss of buoyancy, exposure because of loss of insulating capacity of feathers, and starvation and vulnerability to predators due to lack of mobility [7].
7. Adverse aesthetic effects are fouling of shorelines and beaches. These and other effects have been observed and are documented for petroleum and vegetable oil spills. Case his-

ories discussed in the following section will illustrate some of the harmful effects outlined above.

Some vegetable oils and inedible tallows and greases are characteristically high in free fatty acids (3-30%) [2]. The fatty acids are considered as weak acids because of the limited degree to which they ionize. Their toxicity is dependent on the soluble salt form. Solubility calculations indicate that fatty acids are sufficiently soluble to exceed the toxicity threshold for fish [6,8]. Such salts can be formed in natural waters, but the extent of their formation is dependent on the chemical character of the receiving water. The short-chain and aromatic components of petroleum oil are analogous to the soluble and toxic fatty-acid salts.

In the aquatic environment, a surface film or shore accumulation of unsaturated oils or mixed fatty acids can undergo oxidation-polymerization reactions by contact with air [1]. The process has very similar effects to those observed in the "weathering" of petroleum oils. Although the weathering mechanisms of the two materials are not the same, the hardening of exposed surfaces and the formation of heavy sludges are common to both. The primary processes affecting petroleum oil in the aquatic environment are evaporation of the more volatile constituents, dissolution of the more soluble components and preferential oxidation by microorganisms [3].

Case histories

Oil spills affecting the Minnesota and Mississippi rivers. The largest and most important occurrence to date of a spill of vegetable oil has been the discharge of approximately 2-1/2 million gallons of crude soya and salad oil into the Minnesota and Mississippi Rivers in the winter of 1962-1963 [9]. This spill provided an opportunity for detailed examination of the effects of vegetable oil on the aquatic biota, birds, and mammals. It was spilled into the Blue Edith River, 1/4 mile above the Minnesota River. Because it was winter, the oil moved over and under the ice and congealed or was trapped until the spring.

At the end of March and in early April, the ice thawed and significant amounts of soybean and salad oil went down the Minnesota River to the Mississippi and into its backwaters and lakes. Evidence of oil was found as far as 250 miles downstream from the initial spill site. Dead waterfowl were observed along approximately 60 miles of the Mississippi River, concentrating in lake and backwater areas where the oil became lodged in marshes and on shorelines.

The Minnesota Department of Conservation estimated at least 4,000 and probably more birds died, while another 1,300 were rescued. The causes of death were determined to be several:

1. drowning because of loss of buoyancy when feathers became coated
2. exposure because of loss of insulating capacity of feathers when penetrated by oil
3. starvation and vulnerability to predators caused by loss of mobility in air and water
4. intestinal lesions caused by laxative properties of oil
5. suffocation as a result of nostrils and throat becoming clogged.

All of these effects have also been reported as causes of death for waterfowl destroyed by spills of crude petroleum oil.

Standard 5-day and long-term BOD tests indicated that the crude soya oil had an ultimate BOD of several hundred thousand milligrams per liter. This value, however, applies only to the original oil when it is uniformly dispersed in solution. Under environmental conditions of the spill described above, oils clumped and formed rubbery floating masses instead of dispersing. When oils fail to disperse, large surface areas are not exposed to bacterial action, and the oxygen demand created by the oil does not have a significant effect on the dissolved oxygen concentration unless the dissolved oxygen is already depressed to a dangerously low level by other pollutants. A more serious effect could result in smaller water bodies or when more complete mixing occurs. The floating and settled oil masses or clumps taken from the river or picked up on shore exhibited a relatively slow degradation.

There is also indication that the thick masses of oil which settled on the bottom affected benthic organisms. Support for this conclusion comes from bottom samples taken in April and June. Although the oil content of both samples was similar, the biological activity of the sample taken in June was greatly depressed. This indicates that the settled oil had caused a reduction in the number of benthic organisms probably by smothering or direct toxic effects.

Finally, the spill caused a large number of complaints on aesthetic grounds. The oil covered the shoreline of the rivers and associated lakes, leaving a dark brown residue on beaches, grasses, marshes, and boats. Through oxidation and polymerization the oil sometimes formed a varnish-like crust. The crust was very stable, created an eyesore, and trapped liquid oil which was released later. The displeasing aesthetic effects of this spill lasted more than half a year.

Aeration of Los Angeles Harbor. A refinery was discharging vegetable oil with a BOD of about 10,000 pounds per day to slip number 5 in the Los Angeles Harbor [10]. This, along with an estimated 14,000 pounds of BOD from other sources per tidal change, caused a pollution problem in the harbor. In 1968 a wider program of water quality control was enforced, and it was necessary to provide treatment. To improve the condition of the harbor water, an aeration system was installed and a marked and significant improvement in water quality was produced within 30 days. The air diffuser was anchored to the bottom of the body of water and was held erect by the vertical flow of air. When the air flow was shut off, the diffuser sank to the bottom and thus allowed ships to pass over.

The reduction in BOD was found to be due to two different effects exerted by the aeration system. First, it acted as a mixing device, increasing the dilution factor tenfold. Second, it increased supply of dissolved oxygen by 1 pound of oxygen per horsepower-hour.

A study of fat and oil pollution of New York State waters. In recent years, there has been a growing concern about the pollution of surface waters in New York State by fats and oils [11]. These pollutants have caused difficulties by coating boats and beaches, tainting fish, causing the death of waterfowl, and creating taste and odor problems in water treatment plants. Fat and oil discharges originate from a wide variety of sources including refinery wastes, accidental spillage, construction activities, food and soap manufacturing operations, industrial waste discharges, and sanitary sewage.

Grease-like substances have been found along the shore or floating in Lake Ontario near Rochester, New York. Isolated instances of "grease-ball" contamination have been reported along 50 miles of shoreline east and west of Rochester. The grease balls observed in the vicinity of Rochester in 1965 had the appearance and odor of fat or lard. Samples were analyzed by various techniques in an effort to characterize the composition of the grease balls and to identify the source of the material. They were characterized as mixtures of animal and vegetable fats with similar fatty acid contents.

Distinction between oil and other hazardous substances

The rationale presented in the paper entitled "Oil Versus Other Hazardous Substances" at the 1971 Joint Conference on Prevention and Control of Oil Spills described criteria for distinguishing between oils and potential hazardous substances for the purpose of section 311 of the Federal Water Pollution Control Act of 1970 and 1972 (FWPCA) [12]. These criteria are illustrated in the 1971 paper. They have been a valuable tool for those charged with implementing and enforcing section 311 of the FWPCA. The criteria are applicable to the majority of substances, but not to all.

According to the 1971 rationale, the distinction between a potential hazardous substance and an oil is made on the basis of whether the substance is soluble in an organic solvent such as chloroform or carbon tetrachloride and whether it possesses a defined chemical structure. If the chemical structure is not defined, then the substance is an oil within the meaning of section 311 of the FWPCA. If the chemical structure is defined, then the material is a candidate for designation as a hazardous substance under the same section. The differentiation is important because oils are, by law,

removable whereas hazardous substances may be determined to be nonremovable. Therefore, a discharger is subject to potential civil penalties under the hazardous substances regulations, while he would only be subject to cleanup liabilities under the oil provisions of the law.

Guidelines presented below contain additional considerations in those cases where the previous criteria failed to provide a clear distinction between oils and other materials. For instance, no chemical structure can be written to characterize multicomponent substances such as PCBs, toxaphene, technical grade materials, or mixtures of organic compounds. For these substances, the analysis must be carried further as illustrated in figure 1. If the chemical structure is not defined, a material would qualify as an oil if it meets both of the following criteria:

1. contains mixtures of isomers
2. contains three or more members of an homologous series which differ by a fixed carbon-containing increment

An isomer is defined as a molecule having the same number and kind of atoms as another molecule, but differing from it in respect to atomic arrangement or configuration. An homologous series is a series of organic compounds in which each successive member differs by a fixed increment in certain constituents from the preceding member. For example, CH_3OH (methanol), $\text{C}_2\text{H}_5\text{OH}$ (ethanol), $\text{C}_3\text{H}_7\text{OH}$ (propanol) and $\text{C}_4\text{H}_9\text{OH}$ (butanol) form an homologous series.

If the material does not fulfill both of the above tests, then it does not qualify as an oil but becomes a candidate for hazardous substance designation. The tests must be applied together and do not forbid the separate designation of isomers and homologs as potential hazardous substances.

A candidate for designation as a hazardous substance must fulfill the hazardous substance selection criteria before being so designated, because all nonoil substances are not necessarily hazardous. Under the proposed selection criteria, any element or compound possesses sufficient danger potential to be designated as a hazardous substance if it is lethal to (1) one-half of a test population of aquatic animals in 96 hours or less at a concentration of 500 parts per million (ppm) or less; (2) one-half of a test population of animals in 14 days or less when administered as a single oral dose equal to or less than 50 milligrams per kilogram (mg/kg) of body weight; (3) one-half of a test population of animals in 14 days or less when dermally exposed to an amount equal to or less than 200 mg/kg body weight for 24 hours; (4) one-half of a test population of animals in 14 days or less when exposed to a vapor concentration equal to or less than 200 ppm in air for one hour; or (5) aquatic flora as measured by a 50% decrease in cell count, biomass, or photosynthetic ability in 14 days or less at concentrations equal to or less than 100 ppm.

The major categories of oil are recognized as (1) petroleum or mineral or hydrocarbon oils derived from crude petroleum, (2) mixed fatty acids and fatty oils which are glycerol esters derived from vegetable or animal fats or similar materials, and (3) essential oils derived from plants, usually not esters but more often terpene

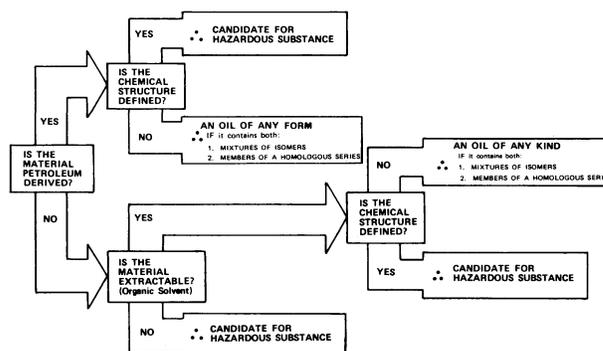


Figure 1. Rationale for distinguishing between oils and materials that may be hazardous substances

hydrocarbons. Materials of category 1 are members of an homologous series in which each successive member has one more CH_2 group in its molecule than the next preceding member. Fats are composed of fatty acids, which are long-chain aliphatic acids, both saturated and unsaturated. Members of category 2 differ by two CH_2 groups. Compounds of category 3 contain multiples of five carbon atoms so related to each other as to allow dissection of their structures into isoprene-like fragments. Oils of all three categories contain multiples of isomers.

For example, kerosene contains as a major constituent straight and branched aliphatic hydrocarbon isomers with carbon numbers mostly in the range of C_{11} to C_{16} . They form three or more members of an homologous series differing by a CH_2 group, and therefore, kerosene qualifies as an oil. Vegetable oil is an edible oil generally composed of mixtures of triglycerides. Because vegetable oils contain isomers of triglycerides composed of three or more saturated and unsaturated straight-chain fatty acids differing by two CH_2 groups in length, they qualify as an oil.

Under these new criteria, PCBs and toxaphene do not qualify as oils, because the members of the homologous series do not differ by a carbon-containing increment. PCBs and toxaphene are composed of a multitude of isomers, and the homologous series increment, instead of containing carbon, is made up of a Cl atom. A mixture of benzene toluene and isomers of xylene qualify as oil under the conditions of the test.

In summary, the guidelines presented here are not intended to replace the rationale published in the 1971 Thompson paper, but rather serve as an adjunct to the previous criteria. Since the publication of the proposed hazardous substances list, this document provides additional guidance in the decision-making process of characterizing borderline materials. In complex cases where the distinction between oil and hazardous materials is not clear, it may still be necessary to have decisions based on such additional considerations as percent composition of mixture, relative degrees of toxicity, and ease of removal.

CONCLUSION

Based on the data presented in this report, parallels can be drawn between animal fats and oils, vegetable oils, fatty acids, and petroleum oils. Because of their common physical and chemical properties, the adverse environmental effects of nonpetroleum oils are strikingly similar to those of petroleum oils. The cited case histories illustrate that the behavior of nonpetroleum oil in the aquatic envi-

ronment is analogous in many respects to the behavior of petroleum oil. Although not specifically mentioned, methods and procedures for the removal of both types of oil from surface waters are also similar. The guidelines for distinguishing between oil and other hazardous materials provide a more broadly applicable distinction for enforcement purposes. All evidence clearly supports the Environmental Protection Agency's position that nonpetroleum oils are subject to the oil regulations under section 311 of the FWPCA.

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