

LISTING WASTE OIL AS A HAZARDOUS WASTE

Report to Congress

This report (SW-909) was prepared by the
Office of Solid Waste as required by section 8(2)
of the Used Oil Recycling Act of 1980 (Public Law 96-463)
and was delivered to Congress on January 16, 1981

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D C 20460

JAN 16 1981

THE ADMINISTRATOR

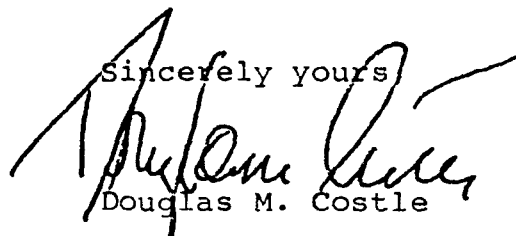
Honorable Walter F. Mondale
President of the Senate
Washington, D.C. 20510

Dear Mr. President:

I am pleased to transmit the Report to Congress "Listing of Waste Oil as a Hazardous Waste" pursuant to Section (8)(2) of the Used Oil Recycling Act of 1980, Public Law 96-463.

The Report presents the Agency's basis for determining that certain waste oils are hazardous wastes according to the criteria promulgated under subsections (a) and (b) of Section 3001 of the Solid Waste Disposal Act, as amended by the Resource Conservation and Recovery Act (RCRA) of 1976. The information presented here will be used later this year to support the proposed listing of these waste oils as hazardous wastes under Section 3001 of RCRA. At that time, the Agency will also promulgate proposed rules under Sections 3002 through 3004 and 3012 of RCRA for the transportation, treatment, storage, disposal, and recycling of waste oils determined to be hazardous wastes.

Sincerely yours


Douglas M. Costle



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

WASHINGTON, D.C. 20460

JAN 16 1981

THE ADMINISTRATOR

Honorable Thomas P. O'Neill, Jr.
Speaker of the House
Washington, D.C. 20515

Dear Mr. Speaker:

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Sincerely yours,

A handwritten signature in dark ink, appearing to read "Douglas M. Costle".
Douglas M. Costle

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INTRODUCTION

This document presents the Administrator's basis for listing waste oil as a hazardous waste. Under Section 3001 of the Resource Conservation and Recovery Act (RCRA), the listing of a solid waste as a hazardous waste brings it under the control of a comprehensive management system which regulates the transportation, treatment, storage, and disposal of hazardous wastes.

Section 3001 of RCRA directs EPA to identify those solid wastes which should be subject to the hazardous waste regulations prescribed under Sections 3002 through 3004 of RCRA. In addition, recognizing the significant threat to human health and the environment posed when used oil* is improperly managed, the Congress passed the Used Oil Recycling Act (P.L. 96-463). Section 8 of this Act requires, no later than January 13, 1981, for the Administrator to: (1) determine whether used oil is a hazardous waste, as defined in Section 3001 of RCRA; and (2) report to the Congress the basis for this determination. The Act also directs EPA, no later than October 15, 1981, to promulgate regulations which protect human health and the environment from the hazards associated with recycled used oil.

The purpose of this document is to present the Administrator's basis for listing certain waste oils (including certain used oils) as hazardous wastes. Later this year, the Agency plans to issue proposed rules to (1) list these oils as hazardous wastes and (2)

* As explained below, used oils are a subset of waste oils.

establish regulations for their transportation, treatment, storage, disposal, and recycling.

DEFINITION OF WASTE OIL

This section describes the universe of waste oil covered in this document. First, this document addresses only petroleum-derived oil. Oils derived from vegetable or animal fats are not included because they are generally not toxic to humans or aquatic life.¹ Additionally, the Used Oil Recycling Act limits the statutory definition of "used oil" to oil derived from petroleum and, thus, it is appropriate for EPA to similarly restrict the regulatory definition of "waste oil".

Second, EPA is defining petroleum-derived oils as those which meet the following three characteristics:

- (1) lack a defined chemical structure;
- (2) contain mixtures of isomers*; and
- (3) contain three or more members of an homologous series which differ by a fixed carbon-containing increment.**

Petroleum-derived wastes meeting the above criteria are defined as waste oils; petroleum-derived wastes not meeting these criteria are

* An isomer is 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 preceeding member. For example, CH_3H (methanol), $\text{C}_2\text{H}_5\text{OH}$ (ethanol), and $\text{C}_3\text{H}_7\text{OH}$ (butanol) form an homologous series.

candidates for designation as "other hazardous wastes"*. This method of distinguishing waste oils from other petroleum-derived hazardous wastes is the same as that used by EPA to implement regulations for oil vs. other hazardous materials under Section 311 of the Clean Water Act (CWA).**2

Finally, this document addresses both unused and used waste oil. Unused oil generally becomes a waste oil when it is spilled, when it mixes with other wastes (e.g., a ship's ballast water), or when it fails specifications for its intended use and is discarded (e.g., ASTM D396 specifications for fuel oils). Used oil becomes a waste oil when it is contaminated with physical or chemical impurities resulting from use, such that the oil cannot be reused for its original purpose without first removing these impurities.

SUMMARY OF LISTING DETERMINATIONS

In regulations prescribed pursuant to Section 3001 of RCRA, solid wastes are listed as toxic hazardous wastes if they contain

* Thus, using this approach, waste automotive crankcase oil is deemed to be a waste oil rather than an "other hazardous waste" because it (1) lacks a definite chemical structure, (2) contains multiples of isomers, and (3) contains members of an homologous series in which each successive member has one more CH₂ group in its molecule than the next preceding member. By contrast, petroleum-derived, waste PCBs are regulated as "other hazardous wastes" rather than as waste oils because the members of the homologous series that they contain do not differ by a carbon-containing increment. The homologous series increment, instead of containing carbon, is made up of a chlorine atom.

** It is important that the regulated community be able to differentiate between waste oils and other petroleum-derived wastes because there will be different requirements under RCRA for these two types of wastes.

any of a number of designated constituents* unless, after consideration of multiple factors, EPA concludes that the waste does not pose a substantial present or potential threat to human health and the environment when improperly treated, stored, transported, disposed of, or otherwise managed. These multiple factors include the type of toxic threat posed; the concentrations of the toxic constituents in the waste; the migration potential, persistence and degradation potential of the toxic constituents; the degree to which the toxic constituents bioaccumulate in ecosystems; the plausible types of improper management to which the waste could be subjected; the quantities of waste generated; damage incidents involving wastes containing the toxic constituents; and actions taken by other governmental agencies with respect to the waste or its toxic constituents.³

Using these criteria, the Administrator has determined that the following waste oils are hazardous wastes, and thus should be subject to the regulations prescribed under Sections 3002 through 3004 of RCRA:

1. Oil spilled to land, and oily debris generated from cleaning-up spills to land or surface water;
2. Used automotive oils; and
3. Used industrial oils.

The exception to this are any of the above waste oils whose petroleum base is white oil.

* These constituents are ones which have been shown in reputable scientific studies to have toxic, carcinogenic, mutagenic, or teratogenic effects on humans or other life forms.

UNUSED WASTE OIL

This chapter first discusses the chemical composition of unused oil. The sources and quantities generated of several categories of unused waste oil, and the management practices typically used to store, treat, recycle, or dispose of it are presented next. This is followed by the Agency's rationale for listing certain unused waste oils as hazardous wastes, including a description of the potential human health and environmental hazards posed by improper management of these waste oils.

I. Chemical composition

The chemical composition of crude oil and refined oil products are described below. As explained later in this chapter, certain constituents in the oil-component of wastes containing unused oil pose a potential threat to human health and the environment when these wastes are improperly managed.

A. Crude oil

Crude oil is not a chemically well-defined substance, but a complex mixture containing literally thousands of compounds, including hydrocarbons, sulfur- oxygen- and nitrogen-containing compounds, and metallo-organic compounds. Although oils from various parts of the world differ widely in their content of the above substances, they are generally divided into three main groups on the basis of their predominant hydrocarbon structure: paraffinic, naphthenic, and aromatic.

Paraffinic (alkanic) crude oils contain mostly saturated straight and branch-chained carbon compounds, along with lesser amounts of cycloalkanes and aromatics. Naphthenic crudes contain

appreciable quantities of compounds with at least one saturated ring structure (cycloalkanes). Aromatic crude oils contain a large concentration of unsaturated benzene ring structures. The varying proportion of these three classes of compounds (alkanes, cycloalkanes, and aromatic hydrocarbons) determine the physical, as well as the chemical properties of crude oils.

Although the relative quantities of these compounds differ in crude oils, an average of the gross compositional data on all world crude yields the following approximate composition for the "average" crude oil:⁴

paraffin hydrocarbons (alkanes)	30%
naphthene hydrocarbons (cycloalkanes)	50%
aromatic hydrocarbons	15%
nitrogen, sulfur and oxygen- containing compounds	5%

Although any specific crude may differ appreciably from these average values, it can be assumed that all crude oils contain some of all three types of hydrocarbons identified above.

B. Refined oil products

Refined oil products (e.g., lubricating oils) also lack constant chemical compositions. The two factors responsible for this variation are crude oil source and the process used to refine the oil. The first factor was described above; the second is discussed below.

A complex combination of inter-dependent processes form the basis of refinery operations. These may include fractionation,

cracking, polymerization, and hydrotreating. The particular combination of processes used at a refinery determines the composition of the final product. For example, catalytic cracking and related conversion processes favor the formation of olefins,* aromatics, and branched paraffins at the expense of other types of hydrocarbons. Solvent treating, on the other hand, removes aromatics, cycloparaffins and olefins.⁵ The processes used at a refinery are chosen based on the type (e.g., fuel oil, lubricating oil) and characteristics (e.g., high octane, low freezing point) of the products that are desired.

Despite the fact that the composition of refined products is highly variable, the following general characterizations can be made. The compounds in refined products are similar to those found in crude oils with the addition of (1) the olefin class of hydrocarbons, and (2) chemical additives** designed to make the product perform more efficiently. Table 1 presents "average" values for the percentage of hydrocarbon compounds found in various refined products.

As noted earlier, a refinery's products may vary significantly from these values, depending on the source of crude oil and the methods used to refine it. And, because the categories in Table 1

* Olefins are straight or branched-chained aliphatic hydrocarbons with at least one double bond. They are used as feedstocks in certain refinery processes (e.g., alkylation and polymerization) to yield high octane blending components for motor gasoline and some jet fuels.

** The additive package differs depending on how the oil is to be used. For example, chemicals added to automotive engine oil to decrease engine knock differ from those added to an oil to lower its freezing point.

TABLE 1
Relative Percentages of Hydrocarbons
in "Average" Refined Oil Products

Petroleum Product	Paraffins	Naphthenes	Aromatics
Motor Gasoline	40-50	30-40	10-35
Jet Fuel	35	50	15
Kerosene	40	45	15
Distillate Fuel Oils	30	45	25-40
Residual Fuel Oils*	15	45	25
Naphtha, Petroleum Solvents	20-35	30-45	20-50
Lubricating Oils and Greases	20-40	30-55	15-45

* includes 15% non-hydrocarbon compounds containing oxygen, nitrogen or sulfur

NOTE: Olefins are often not measured, although they are present in most products to some degree

Source: reference 4, p. 86.

are quite broad, there are instances where the "average" values for a particular category do not reflect the composition of certain groups of hydrocarbons within a category*. However, the table is useful because it illustrates that, like crude oils, most refined products contain significant quantities of all three classes of hydrocarbons (i.e., alkanes, cycloalkanes, and aromatic).

II. Sources and Management Practices

Most unused waste oil fits into three general categories:

(1) spilled oil, (2) oily waste from tank-cleaning and deballasting operations, and (3) oil unfit for its intended use because it has been improperly handled or fails to meet specifications. These three sources of unused waste oil are discussed below.

A. Spills

Surface Water: About 10,000 oil spills totalling 10 to 20 million gallons of oil enter the territorial waters of the United States every year.⁶ Through the provisions of the National Oil and Hazardous Substances Pollution Contingency Plan**, the National Response Team*** ensures that appropriate cleanup operations of this spilled oil are undertaken by the discharger or by federal, state, or local authorities. Removal of the spilled oil from

* E.g., white oils, which are a subset of the "lubricating oils and greases" category, are refined such that they contain essentially no aromatic hydrocarbons. Therefore, the "average" value of 15 to 45 percent aromatics is inaccurate for white oils.

** This plan is designed to guide federal spill response actions under Section 311 of the CWA.

*** The National Response Team is a multi-agency organization responsible for oil spill contingency planning at the national level.

surface waters results in the creation of an oily debris which must be disposed of. Currently there are no federal regulations controlling the treatment, storage, or disposal of the oily debris resulting from these cleanup operations.

Efforts by emergency response teams to locate adequate sites to manage (i.e., store, treat, or dispose) oily debris are often frustrated. Local residents are always anxious to have the debris removed from sight, but frequently are unwilling to allow it to be disposed of in their sanitary landfills. Citizen opposition is even worse when neighboring communities are asked to accept another's debris, regardless of whether their landfill is better able to contain it.

Because of the intense emotional atmosphere associated with oil spill cleanup, the resulting oily debris must often be temporarily stored until an appropriate site is found. Sometimes, either because of citizen pressure or the absence of a suitable nearby site, the debris is disposed of in a landfill which is inadequate to contain it.*⁷

Land: The Coast Guard and EPA receive notification of only oil spills that:

cause a film or sheen upon or discoloration of the surface of the water or adjoining shorelines or
cause a sludge or emulsion to be deposited beneath the surface of the water or upon adjoining shorelines.

(40 CFR Part 110).

* There is growing recognition among local officials that the time to identify appropriate sites to dispose of oily debris is before rather than after an oil spill occurs. To encourage this type of advance planning, EPA has prepared a detailed, how-to-do-it manual (EPA-600/7-80-016) and an accompanying film for oil spill debris disposal for state and local officials.

Oil spills also occur to land. They are typically caused by tank failures, pipeline ruptures or leaks, spillage during transfer from one container to another, and indiscriminate dumping. Because the Agency has no reporting requirements for these spills, it is difficult to estimate the quantity of waste oil generated from them. However, several states require persons to file reports on oil spills to the land as well as water. The following is a summary of data collected in these reports.

MAINE: Nearly 90,000 gallons of oil were spilled in Maine in 1979. Table 2 illustrates the environmental media (i.e., surface water, ground water, or land) affected by these spills. Although the majority of the spills entered surface water, a significant number occurred on land. Note also that several of the spills resulted in ground-water contamination.⁸

MICHIGAN: During 1976, approximately 500 spills to ground water were reported to the Michigan Department of Natural Resources. The largest of these was a spill of 360,000 gallons of fuel oil.⁹

NEW HAMPSHIRE: Table 3 summarizes the reported oil spills that occurred in New Hampshire over the past six years. Note that of the 219,368 gallons of oil spilled during that period, nearly half of the oil spilled on land.¹⁰

NEW YORK: 4,287 oil spills totaling over 9 million gallons were reported to New York's Department of Conservation from January, 1976 to September, 1979. Approximately 25% of these spills occurred on land, involving over 1.5 million gallons. New York's records indicate that 238,983 gallons of the oil spilled on the ground was not cleaned up.¹¹

While not comprehensive, data from these few states indicate that the amount of oil generated from spills to land is significant and, therefore, should not be overlooked when assessing the magnitude of the potential environmental threat posed by unused waste oil.

TABLE 2

State of Maine

Environmental Media Affected by Spills in 1979

<u>Medium Affected</u>	<u>Number of Spills</u>
Land	95
Surface Water	153
Land to Surface Water	66
Ground Water	6
Ground Water to Surface Water	17
Land to Ground Water	4
	<hr/>
Total Spills	341

Source: reference 8.

TABLE 3
State of New Hampshire
Oil Spill Summary for 1975-1980

Year	# Spills Reported	TO LAND			TO WATER		
		# Spills	Gallons Spilled	(#)*	# Spills	Gallons Spilled	(#)*
'75	45	12	19632	(2)	33	22335	(12)
'76	53	17	23441	(4)	36	19430	(21)
'77	52	13	6210	(4)	39	6687	(23)
'78	59	11	8855	(2)	48	30323	(21)
'79	79	27	27985	(10)	52	29692	(33)
'80**	52	23	15816	(7)	29	8962	(17)
Total			101939			117429	

*(#) Indicates number of spills with an unestimated amount
of spilled oil

** Through November, 1980

Source: reference 10.

Unlike oil spilled to surface water, oil spilled to land is not subject to federal regulation (unless it ultimately reaches surface water) and, therefore, its cleanup is not supervised by a federal organization comparable to the National Response Team. In fact, there is no federal law which even requires oil spilled to land to be removed from the ground.

Some states send officials to oversee cleanup operations of large oil spills to land. But, in most cases, the treatment, storage, and disposal of oily debris resulting from this type of spill is not subject to control.

B. Vessel Operations

Ships and vessels generate two types of wastewaters which contain unused waste oil: ballast water* and tank cleaning water**.

The discharge to surface water of ballast and tank-cleaning water is subject to regulations (33 CFR Part 157) administered by the Coast Guard. If oily water is brought ashore (as is often done during deballasting operations), it is usually first pumped to on-shore storage tanks, and ultimately released to refinery wastewater treatment plants. Oil recovered onboard from tank-cleaning water is generally used as a feedstock at oil refineries

* Ballast water: After crude oil or petroleum products are off-loaded from a tanker, water or seawater is pumped into the vessel's storage tank to maintain stability. Oil adhering to the tank's wall mixes with the water as a result of ship motion, thus creating an oily wastewater.

** Tank-cleaning water: Before a change in fuel oil cargo is made, cargo tanks are washed. Oily wastewaters generated by tank cleaning are either added to a ship's ballast water or processed through an oil-water separator. In the latter case, water which has passed through a separator is discharged at sea, whereas the oil component is retained on-board and is eventually brought ashore.

when it is brought ashore.¹²

Of the unused waste oil generated onboard vessels, nearly 300 thousand metric tons of it are discharged to surface waters each year.¹³ The Agency has no data on the quantity of waste oil brought ashore in ballast and tank-cleaning waters.

C. Inadequate Handling or Formulation

Unused oil may become unsuitable for its intended use and, thereby, a waste oil when it is improperly handled. An example of this occurred in North Carolina in 1978 when several barrels of the federal government's automotive lubricating oil could not be used in its military vehicles because the oil had been stored for longer than its recommended shelf life.*¹⁴

Unused oil may also become waste oil if it is formulated in a way that does not meet specifications for its intended use. Oil purchased by the government, for example, must meet certain specifications. These specifications differ depending on how the oil is to be used (e.g., the requirements for fuel oil differ from those for lubricating oil). If oil is 'off-spec', it is generally returned to the seller. The oil can then either be re-formulated, sold for another use, or disposed of.

The Agency has no data on how much of these types of unused waste oil are generated, nor on how they are ultimately reused or disposed of.

* The oil was ultimately given to a state-operated re-refinery to be used as a feedstock for lubricating oil.

III. Basis for Listing

A. Adverse effects of crude oils and refined products

Crude or refined oils are the major component of the unused waste oils described earlier. In this section, the toxic effects of these components are discussed, first with respect to aquatic organisms and, second, with respect to humans. This is followed by a brief description of the organoleptic (taste and odor) properties of oil-tainted ground water.

1. Aquatic Environment

EPA has already established that oil discharged to surface water poses a significant threat to the environment. In response to a court challenge in 1974, EPA successfully defended its position that an oil spill sufficient to produce a film or sheen* on the surface of the water is large enough to cause harm to the environment.¹⁵ In its deposition (see Appendix 1), EPA documented that oil produces a harmful effect on aquatic organisms not only by physically coating them, but also by causing adverse chemical changes within the organism.

Appendix 4(a) of this deposition includes descriptions of the following types of damage to aquatic organisms caused by floating oily layers: inability of ducks to swim or dive for food in the presence of oil films; loss of insulating ability of feathers contaminated with oil and subsequent loss of normal body temperature and death; reduced viability of duck eggs due to oil-soaked plum-

* An oil layer at least 150 nanometers thick (1 nanometer = 1 billioneth of a meter), or 39.37 billioneths of an inch, is required to produce such a sheen.

age; and pneumonia and gastro-intestinal irritations in waterfowl following preening of oil-coated feathers.

Appendices 4(b), 5 and 6 of the deposition document some of the adverse physiological changes to aquatic organisms resulting from small spills of oil to surface water. Harmful effects cited in these appendices include: inhibition of marsh grasses to reproduce; blocked chemoreception in fish larvae; increased susceptibility of seagrasses to parasites; abnormal development of herring larvae; and the killing of various organisms including copepods, shrimp, and white mullet.

The deposition's claim that oil poses a significant threat to the environment when discharged to surface water is supported by information presented in Tables 4 and 5. Table 4 is a compilation of data on the lethal toxicity of various oils to aquatic organisms.¹⁶ The table is presented here for two reasons. First, to confirm that low concentrations of oil can be lethal. And second, to point out that, in nearly all cases, oil's water soluble hydrocarbons (aromatic) are toxic at lower concentrations than the other components or types of oil listed in the table.

Table 5 summarizes the sublethal effects of crude oil and refined oil products on aquatic organisms.¹⁷ The purpose of including the table in this document is to re-emphasize that the sublethal effects of oil are significant (e.g., disruption of feeding, breeding, and locomotive behavior; interference with thermoregulation; etc.), and that the concentrations necessary to bring about these effects are often very small.

TABLE 4

Summary of lethal toxicities of various petroleum products to aquatic organisms
(a thorough discussion of duration and test conditions is found in Moore, Dwyer, and Katz, 1973)

Type organism	Soluble H-carbons	Dispersants	±2 Fuel oil/ Kerosene	Fresh crude	Gasoline	Diesel fuel	Refinery effluents	Waste oil	Lubricants	Residuals	Weathered crude
Marine Flora	10 ppm ^{20*} - 650 ppm ^{20*}	1.2 ppm ^{20*} - 313 mg/l [ppm] ²¹	<100 ul/l [ppm] ²¹	Toxic to many salt marsh plants. ²¹				10 ppm ¹⁴			Coating more significant than lethal toxicity. ²⁰
Finfish.....	5 ppm ^{20*} - 50 ppm ²⁰	1 ppm ^{20*} > 10,000 mg/l [ppm] ²⁰	550 ug/ml [ppm] ²⁰	88 mg/l [ppm] ²⁰ 18 ml/l [x 10 ³ o/oo]	91 ppm ²⁰	204-420 ppm ²⁰		1,700 ppm ¹⁴		2,000-10,000 mg/l[ppm] ²⁰	
Larvae and Eggs.....	0.1 ppm ^{20*} - 1 ppm ^{20*}	1 ppm ^{20*} - 42 ppm ²⁰	0.1 ul/l[ppm] ²¹ 4 ug/ml [ppm] ²¹	0.1 ul/l[ppm] ²¹ 100 ppm ^{20*}				1->25 ppm ¹⁴		No effect reported. ²⁰	
Pelagic Crustacea....	1 ppm ^{20*} - 10 ppm ^{20*}	5 ppm ^{20*} - 100 ppm ²⁰	5 ppm ^{20*} - 50 ppm ²⁰	0.1 ml/l [x 10 ³ ppm] ²⁰ 40 ppt [x 10 ³ ppm] ²⁰				15->50 ppm ¹⁴			
Benthic Crustacea....	1 ppm ^{20*} - 10 ppm ^{20*}	2 ppm ^{20*} - 100 ppm ²⁰	5 ppm ^{20*} - 50 ppm ^{20*}	0.56 mg/l [ppm] ²¹						>10,000 ppm ²⁰	
Gastropods....	10 ppm ^{20*} - 100 ppm ^{20*}	5 ppm ^{20*} - 2,000 ppm ²⁰	50 ppm ^{20*} - 500 ppm ^{20*}	Toxicity re- ported for several species, but concentra- tion given ²⁰						No effect reported. ²⁰	
Bivalves....	5 ppm ^{20*} - 500 ppm ²⁰	0.5 ppm ^{20*} - 100 ppm ²⁰	30-40 ml/l [x 10 ³ ppm] ²¹	1 ml/l [x 10 ³ ppm] ²¹ 10 ² ppm ²⁰						Incorpora- tion. ²⁰	
Other Benthic Invertebrates	1 ppm ^{20*} - 10 ppm ^{20*}	5 ppm ^{20*} - 100,000 ppm ²⁰	5 ppm ^{20*} - 50 ppm ^{20*}	100 ppm- 6,100 ppm ²⁰						1,952-2,417 mg/l[ppm] ²¹	
Freshwater Finfish.....	5.6 ppm ¹¹ - 4,924 ppm ²⁴	10 ppm ²¹	1,000-150,000 mg/l[ppm] ²⁰	0.3 mg/l [ppm] ¹² 500 mg/l [ppm] ²⁰	40 mg/l [ppm] ²⁰ 180 mg/l [ppm] ²¹	160-4,000 mg/l[ppm] ²¹	160-4,000 mg/l[ppm] ²¹	~39 ppm ¹³	3,000-180,000 mg/l[ppm] ²¹		
Freshwater Flora.....		200 ppm ²¹									
Mammals & Birds.....	Most lethal (or sublethal) effects are caused by physical coating, entanglement, ingestion of fine oil droplets, or incorporation of hydrocarbons through food chains										

Note: (1) Numbers in brackets represent reported values (volume to volume or weight to volume basis) converted to ppm.

(2) Superscript numbers refer to references.

(3) Asterisks indicate values estimated by Moore, Dwyer, and Katz, 1973. (However, estimates are supported by examples given therein).

(4) In some cases, the above values have been taken from summary type presentations (for example: Moore, Dwyer, and Katz, 1973), the corresponding reference numbers therefore do not necessarily refer to the original publication.

(5) The manner in which the above values are reported is only an attempt to exemplify the ranges in threshold lethal toxicities, based on some of the existing published data, and should therefore not be regarded as absolute limits of toxicity for a given category of toxicant or test organism. It must be understood that there exist numerous additional published data that fall within the ranges suggested above, and possibly data that may suggest further widening these ranges. It is not the author's intention to herein summarize all of the toxicity values reported thus far for petroleum and petroleum products.

TABLE 5

—Summary of some sublethal effects of petroleum products on marine life—Continued

Type organism	Species	Reference	Type petroleum product	Concentration	Sublethal response
Fish	Barnacle larvae (<i>Balanus balanoides</i>)	Mironov, 1970	"Oil"	10-100 ul/l (ppm)	Abnormal development
	Crab larvae (<i>Pachygrapsus marmoratus</i>)	Mironov, 1970	"Oil"	10-100 ul/l (ppm)	Initial increase in respiration
	Chinook salmon (<i>Oncorhynchus tshawytscha</i>)	Rocksen & Bailey, 1973*	Benzene	5,10 ppm	Initial increase in respiration
Crustaceans	Atlantic silversides <i>Menidia menidia</i>	Gardner, et al. 1973	Crude (whole fractions) (water soluble) (water insoluble)	140 ppm (v/v) 12 ppm estimated 588 ppm (v/v)	Histological damage to chemoreceptors
	Lobster (<i>Homarus americanus</i>)	Blumer, et al. 1973	Crude, kerosene	10 ppm	Effects on chemo-reception, feeding times, stress behavior, aggression
	Pollicipes <i>polymerus</i>	Straughan, 1971	Crude—Santa Barbara	Field study after blowout	Apparent decrease in adult breeding; no recruitment in oiled areas
	Lobster (<i>H. americanus</i>)	Atema & Stern, 1972	La Rosa crude	Extracts	Delay in feeding
	<i>Pachygrapsus crassipes</i>	Kittredge, 1971*	Crude	Dilutions of diethyl ether extracts (1:100)	Inhibition of feeding
	<i>Uca pugnax</i>	Krebs, 1973*	No. 2 fuel oil	Field observations after W. Falmouth spill	Adverse effects on sexual behavior
Molluscs	Mussel (<i>Mytilus edulis</i>)	Gillfillan, 1973*	Crude	1 ppm	Reduction in carbon budget (increase in respiration, decrease in feeding)
	Snail (<i>Nassarius obsoletus</i>)	Blumer, et al. 1973	Kerosene	Saturated extract diluted 10 ¹⁰	40% reduction in chemotactic perception of food
	Snail (<i>Nassarius obsoletus</i>)	Jacobson & Boylan, 1973	Kerosene		
	Clim (<i>Mya arenaria</i>)	Barry & Yevich, 1974	No. 2 fuel oil	Collected from field	Gonadal tumors
	Oyster (<i>Crassostrea virginica</i>)	Mackin & Hopkins, 1961	Bleedwater		Reduced growth and glycogen content
	Snail (<i>Littorina littorea</i>)	Perkins, 1970*	BP 1002	30 ppm	Significant inhibition to growth
	Oyster (<i>Crassostrea virginica</i>)	Menzel, 1948; in Nelson-Smith, 1973	"Oil"	0.01 ppm	Marked tainting
	Mussel (<i>Mytilus edulis</i>)	Blumer, et al. 1971*	No. 2 fuel oil	Collected from field after spill	Inhibition in development of gonads
Other benthic invertebrates	Polychaeta (<i>Capitella capitata</i>)	Bellan, et al. 1972 ¹	Detergent	0.01-10 ppm	Decrease in survival, fecundity

Note: *1 taken from National Academy of Sciences, 1973.

*2 taken from Moore, Dwyer and Katz, 1973.

TABLE 5 (Cont'd)

—Summary of some sublethal effects of petroleum products on marine life

Type organism	Species	Reference	Type petroleum product	Concentration	Sublethal response
Marine flora	Phytoplankton (<i>Chlorocella vulgaris</i>).....	Knauss, et al. 1972 ²	Crude Naphtalene	1 ppm 3 ppm	Suppress growth; reduction of bicarbonate uptake
	Phytoplankton (diatoms and dinoflagellates)	Mironov, 1970 ^{1,2}	"Oil"	10 ⁻¹ 10 ⁻⁴ ppm	Inhibition or delay in cellular division
	Phytoplankton (<i>Asterioniscia japonica</i>).....	Aubert, et al. 1969 ¹	Kerosene	3 ppm; 38 ppm	Depression of growth rate
	Phytoplankton (<i>Phaeodactylum tricornutum</i>).....	Lacaze, 1967 ¹	Kuwait crude	"1 ppm"	Depression of growth rate
	Phytoplankton (<i>Monochrysis lutheri</i>).....	Strand, et al. 1971 ¹	Kuwait crude; dispersant emulsions	20-100 ppm	Inhibition of growth; reduction of bicarbonate uptake at 50 ppm
	Phytoplankton (<i>Phaeodactylum tricornutum</i> , <i>Skeletonema costatum</i> , <i>Chlorocella sp.</i> , <i>Chlamy- domonas sp.</i>).....	Nuzzi, 1973 ¹	Extracts of outboard motor oils, No. 6 fuel oil, No. 2 fuel oil		
	Phytoplankton.....	Gordon and Prouse, 1973 ¹	Venezuelan crude, No. 2 and 6 fuel oils	10-200 mg/l(ppm)	Stimulation of photo- synthesis at 10-30 mg/l; decrease in photo- synthesis at 100-200 ug/l No. 2 fuel oil
Larvae and eggs:	Kelp (<i>Macrocystis angustifolia</i>).....	Wilber, 1968 ²	Toluene	10 ppm	75% reduction in photosynthesis within 96 hours
	Lichen (<i>Lichen pygmaea</i>).....	Brown, 1972 ¹	Kuwait crude, BP1002	0.1-100 ppm	1 ppm emulsifier decrease; total C ¹⁴ fixation
	Pink salmon fry (<i>Oncorhynchus gorbuscha</i>).....	Rice, 1973	Prudhoe Bay crude	16 ppm	Avoidance effects; cou have effect on migration behavior
	Black Sea turbot (<i>Rhombus maeoticus</i>)..	Mironov, 1967	"Oil"	0.01 ppm	Irregularity and delay in hatching; resulting larvae deformed and inactive
	Plaice larvae (<i>Pleuronectes platessa</i>).....	Wilson, 1970 ¹	BP 1002	0-10 ppm	Disruption of feeding behavior
	Cod fish larvae (<i>Gadus morhua</i>).....	Kuhnhold, 1970 ¹	Iranian crude	Aqueous extracts from 10 ³ ppm, 10 ⁴ ppm	Adverse effect on behavior, leading to death
	Lobster larvae (<i>Homarus americanus</i>).....	Wells, 1972 ¹	Venezuelan crude	6 ppm	Delay molt to 4th stage
	Sea Urchin larvae (<i>Strongylocentrotus purpuratus</i>).....	Allen, 1971 ¹	Extracts of Bunker C	0.1-1 ppm	Interference with fertilized egg development

2. Human Health

There are several substances listed in Appendix VIII of 40 CFR Part 261 that are present in oil's aromatic or water soluble fraction. These include naphthalene, phenols, benzene, benz(a)anthracene, and benzo(a)pyrene. The last three have been identified by EPA's Carcinogen Assessment Group as exhibiting substantial evidence of carcinogenicity. Detailed discussion of the toxic and carcinogenic effects of these substances are contained in the Agency's water quality criteria documents prepared under Section 304(a)(1) of the CWA.¹⁸

The substances listed in Appendix VIII have been shown to have toxic, carcinogenic, mutagenic or teratogenic effects on humans or other life forms. The presence of any of these constituents in a solid waste is presumed to be sufficient to list the waste as a hazardous waste unless, after consideration of designated multiple factors, EPA concludes the waste is not hazardous.¹⁹ These multiple factors were described earlier (see page 4).

Table 6 presents the relative concentration of some of these substances in both crude oils and certain refined oil products. The authors of the table found that benzene, naphthalene and phenols accounted for about 90% by weight of the identified organics in the water soluble fraction of samples of crude and #2 fuel oil. For bunker C fuel oil, phenols and naphthalenes were among the most abundant class of compound found, with each present at a concentration of about 1 mg/l.²⁰

TABLE 6
Water Soluble Components of
Crude and Refined Oils

Compound Class	Crude (4 samples)	#2 Fuel (5 samples)	Bunker C (1 sample)
* Benzene	+++	+++	+
Indans	++	++	+
* Naphthalenes	+++	+++	++
Tetralins	++	++	+
Biphenyls	+	+	+
Anilines	-	++	-
Quinolines	-	-	++
Indoles	-	++	+++
Benzothiophes	+	+	+
* Phenols	+++	+++	+++
Phthalides	-	-	-
Benzaldehydes	-	-	-
Aromatic Ketones	-	+	-

+++ = High relative concentration

++ = Low relative concentration

+ = Trace amounts

- = Not detected

* = Substances listed in Appendix VIII of 40 CFR Part 261

NOTE: Although no absolute concentrations (i.e., ppm) for most of these substances were given, the levels for phenols and naphthalenes in Bunker C fuel oil were reported to both be about 1 ppm. Thus, it seems likely that substances with relative concentrations of (+++) have absolute concentrations in the ppm, as opposed to the ppb range.

The fact that carcinogens are found in oil is especially important in determining whether oil-containing solid wastes are hazardous wastes. EPA has in the past employed the assumption that carcinogenicity is a non-threshold phenomenon. As such, "safe" or "no effect" levels for carcinogens cannot be established because even extremely small doses will elicit a finite increase in the incidence of cancer. Accordingly, the water quality criteria promulgated under Section 304(a)(1) of the CWA state that, for maximum protection of human health, the ambient water concentrations for carcinogens should be zero.*²¹

Similarly, under RCRA, the fact that a solid waste contains known or proven carcinogens generally is sufficient cause to list the waste as hazardous, unless there is strong indication that the waste's constituents will not migrate and persist if the waste is improperly managed.²²

Of the carcinogens present in oil, benzo(a)pyrene or BaP is a highly potent carcinogen. It has been reported to be present in crude oil and refined oil products.²³ Because the BaP molecule is hydrophobic, it will partition preferentially into lipids, where it is subject to both bioaccumulation and biomagnification effects.²⁴ Samples of crude oil from the Persian Gulf, Libya, and Venezuela have been found to contain 400, 1,320, and 1,600

* However, because zero concentration may not be attainable at the present time, the criteria specify ranges for carcinogens associated with incremental cancer risks. Cancer risk levels provide an estimate of the additional incidence of cancer that may be expected in an exposed population. A risk of 10^{-5} for example, indicates a probability of one additional case of cancer for every 100,000 people exposed; a risk of 10^{-6} indicates one additional case of cancer for every million people exposed, and so forth.

ug/kg respectively of BaP.*25

Data on other levels of carcinogens found in crude oils (e.g., benz(a)anthracene) are scarce. It has been estimated, however, that the carcinogenic hydrocarbon content of crude oils generally falls within the 100 to 1,000 ug/kg range.²⁶

Data on the carcinogenic hydrocarbon content of refined oils is also limited. However, unless an oil product has been refined with processes that remove aromatic hydrocarbons (e.g., solvent washing), it can be assumed that the product will contain carcinogens similar to those found in the parent crude. In fact, since most refining processes enrich rather than diminish the aromatic content of refined products relative to the crude oils from which they are derived, it is likely that the carcinogenic hydrocarbon content of most refined products is at least as high as that of crude oils. For example, the level of benzene found in motor gasolines generally exceeds 10,000 ppm.**27

The above substances are harmful whether ingested from surface water or ground water, and thus aquatic organisms as well as humans could be adversely affected by consuming oil-tainted surface water

* At the 10^{-6} cancer risk level, the ambient water quality criteria for protection of human health from chronic exposure are 2.8 ng/l (parts per trillion) for both benzo(a)pyrene and benz(a)anthracene.

** Benzene is known to cause leukemia and other adverse effects in humans at concentrations of 25-100 ppm (see Industrial Union Dept., AFL-CIO v. American Petroleum Institute, U.S. , (July, 1980) (slip op. at 7, 20-21, reviewing regulations of the Occupational Safety and Health Administration).

At the 10^{-6} cancer risk level, the ambient water quality criteria for protection of human health from chronic exposure is .66 ug/l (parts per billion) for benzene.

or ground water. However, because the previous section already documented the harmful effects that oil in surface water has on aquatic organisms, the following discussion will focus on the potential threat to human health posed by ingestion of these substances in oil-contaminated ground water.

Two factors play a significant role in determining the toxic effects of oil in ground water: the types of hydrocarbons the oil contains, and the solubility of these hydrocarbons in water.

To begin with, the more reactive a compound, the more likely it will be to interfere with biological functions. The probable mechanism whereby hydrocarbons exert this interference is through cell membrane disruption and incorporation.²⁸ The relative reactivity and, hence, toxicity of the classes of hydrocarbons found in oil increases from paraffins to naphthenes to olefins to aromatics.²⁹ Oils containing a predominance of aromatic compounds are generally more toxic than those containing mostly paraffinic or naphthenic hydrocarbons.^{30, 31} Note that the Appendix VIII substances described earlier are all aromatic hydrocarbons.

As discussed in more detail below, the solubility of the hydrocarbons in oil is also a significant factor in determining the effects of oil in ground water. Unless these hydrocarbons are water soluble, they may either never reach ground water or will not mix with it sufficiently to pose a threat to humans that use it. The water solubility of hydrocarbons also increases from paraffins, to naphthenes, to aromatics.³² Benzene, for example, has a saturation solubility of 1,800 ppm in distilled water, as compared to about

10 ppm for the alkane of equivalent molecular weight.*³³ Thus, the aromatic portion of oil tends not only to be the most toxic, but is also the most likely to migrate to ground water.

Toxicological data on oil ingestion by humans and other non-aquatic organisms is scarce. The Agency is unaware of any studies on the effects of crude oils on terrestrial organisms. Research on the effects of refined oil products is also scant. However, the small amount of research that has been conducted on refined oils offers some insight into the potential adverse effects of all oils on terrestrial organisms, including humans.

Toxicity Studies

This discussion deals with three types of refined oil: middle distillate fuels, lubricating oils, and white oils. The middle distillate category includes kerosene, diesel fuel, and fuel oils No. 1 and 2. The general hydrocarbon composition of this category of oil is shown in Table 7.

Table 8 summarizes the general hydrocarbon composition of lubricating oil stocks. Like the middle distillates, lube oils generally contain all three types of hydrocarbons. However, because aromatic hydrocarbons produce poor viscosity characteristics and are unstable towards oxidation, some or all of these aromatics are often removed from lube oil stocks. The degree to which the aromatics are removed depends upon the use to which the oil is to

* Solubility is also a function of molecular weight (i.e., solubility increases as molecular weight decreases). This is why compounds of similar molecular weights are compared when assessing the effect of hydrocarbon type on solubility.

TABLE 7
Variation in Hydrocarbon Composition of Middle Distillates

Hydrocarbon type	Range (in wt. %)	a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p
Reported values (in wt.%)																	
Saturated paraffins	37-43			60	35	25	-	74	71-76	75	60	78.9	72.8	72.6	77	50	80.4
	34.6-90		34.6	30	55	50	65						14				
Cycloparaffins	26-32																
Aromatics	30-32		57.5	10	15	25	33	26	24-29	25	40	19.5	58	27	23	50	19.6
Unsaturates	0-7.5	-	7.5	-	-	-	2	-	-	-	-	1.6	5.2	0.4	-	-	-

a = Fuel oil No. 2; b = Cracked middle distillate; c = Paraffin-base kerosene; d = Paraffin-base middle distillate; e = Aromatic-base kerosene; f = Aromatic-base middle distillate; g = Diesel fuel; h = Diesel fuel; i = Straight-run diesel fuel; j = Middle distillate; k = Diesel fuel; l = Fuel oil No. 2; m = Diesel fuel; n = Straight-run middle distillate; o = Cracked middle distillate; p = Middle distillate.

TABLE 8

Hydrocarbon Composition of
Lubricating Oil Stocks

<u>Hydrocarbon Type</u>	<u>Percent</u> (by weight)
Alkane	45-76
Cycloalkane	13-45
Aromatic	10-30

TABLE 9

Hydrocarbon Composition of
White Mineral Oils

<u>Hydrocarbon Type</u>	<u>Percent</u> (6 samples)
Straight and branched alkanes	26.8
Cyclic alkanes	
noncondensed (1 ring)	26.8
condensed	
2 rings	22.1
3 rings	13.6
4 rings	6.7
5 rings	2.9
6 rings	0.9
Aromatic hydrocarbons	0

Sources: reference 5, pg. 20 for Table 8:
reference 5, pg. 23 for Table 9

be put. Lube oils from which all aromatic hydrocarbons are removed are called white oils. White oils are transparent, colorless and odorless and tasteless when cold. They are used for medicinal purposes, as food additives, as finishing oils, and other uses requiring a very pure lubricant. Table 9 provides the general composition of white oils.

The point to remember about the chemical composition of these oils is that white oils contain no aromatics, whereas the middle distillates and lube oils do. The toxic effects on terrestrial organisms to each of these three types of oil is discussed below.

The majority of the literature on oil toxicity to terrestrial organisms stems from a concern for workers exposed to oil while performing their jobs. Workers are usually exposed to oil either when it splashes from machinery onto their bodies, when they lean against oil-coated machines, or when they inhale oil mists (generated when oil contacts hot pieces of machinery). Studies conducted on humans and test animals therefore, tend to focus on dermal or aerosol exposure to oil. Few occupations call for the oral ingestion of oil and, consequently, little data has been collected on this mode of exposure. The exception to this is data collected on white oils. Because white oils are used as laxatives, their biomedical effects when ingested by humans and test animals have been studied.

Data on human toxicity to the three types of oil will be presented first.*

* All damage incidents taken from reference 5.

Middle distillates

Acute skin contact with kerosene soaked clothing caused severe epidermal necrolysis in a 12-year old boy. Extensive erythema and detachment of epidermal tissue overlying a purulent exudate occurred. Skin patch tests with kerosene for 24 hours caused skin irritations of varying degree in humans; a highly aromatic middle distillate fuel produced the strongest skin irritation.

A worker who swallowed fuel oil during a siphoning procedure developed acute gastritis with hematomesis. Gastric mucosal lesions, observed on X-ray, healed in about 1.5 months. Intense gastrointestinal irritation has been noted after kerosene swallowing.

Diesel fuel ingestion by young children often causes pneumonia, due to entry of the fuel into the lungs (i.e., aspiration pneumonitis). Cough, dyspnea and a blood-tinged frothy discharge have been noted in these cases.

Extensive bilateral pulmonary necrosis and gangrene occurred in a 44-year old man who aspirated diesel fuel.

Folliculitis, furuncles, pyoderma, abscesses and papular eruptions have been reported due to repeated exposures to diesel fuel.

Lubricating oils:

Squamous cell carcinoma of the hands, face, and groin after chronic oil exposure in industry has an occurrence which parallels the degree of refining an oil underwent prior to use. The polycyclic aromatic hydrocarbons present in all but white oils are believed to be responsible for their carcinogenicity.³⁴

Cases of skin cancer due to petroleum oil used in industries such as cotton mule spinning and metalworking reached a peak in 1928 and declined slowly by 1945. This is due to the introduction of concentrated sulfuric acid washing in the 1930's and later on, solvent extraction, which removes polycyclic aromatics from lubricating oils.*

* The degree of washing (either acidic or solvent) determines the amount of aromatics remaining in the oil.

The following are data collected from two studies on lube oil-induced skin cancer:

In Great Britain, skin cancer studies have revealed that over 86% of skin cancer cases that could be traced have been found to occur in association with oil exposure, although the type of oil was not related to incidence.

In France, in a study conducted on 5,000 workers exposed to lubricating oils and oil aerosols, it was found that the scrotal skin cancer rate for these workers was 36 times higher than that of the general unexposed population.

White oils:

Ingestion of white mineral oil, as a laxative, causes lubrication of the rectal sigmoid. The oil prevents absorption of fat soluble vitamins A, D, E, and K, with resultant problems related to deficiencies of these vitamins (alteration of calcium and phosphorous metabolism through interference with vitamin D absorption; hypoprothrombinemia due to interference with vitamin K absorption). It also coats particles of food in the intestine, interfering with absorption, and sometimes contributing to severe weight loss.³⁵

Nonetheless, the Food and Drug Administration allows the use of mineral oil in food, subject to stringent quality and quantity standards.*

* These standards include provisions which regulate:

1. the quality and quantity of white mineral oils added to food for human consumption.
2. the use of mineral oil as a component of non-food articles which come in contact with food for human consumption (21 CFR Part 178). These standards restrict oils that can be used for this purpose to white oils. The quality and quantity limitations prescribed in Part 172 for white oils are incorporated by reference in these rules for non-food articles.
3. the addition of mineral oil to animal feed. Quality and quantity specifications are prescribed for using white oils for this and other animal-related purposes (CFR Part 573).

Bronchial inflammation, distortion, and plugging with oil has been observed in persons who have aspirated white mineral oil. The symptoms of oil pneumonia are non-specific, but include dyspnea, cough, wheezing, and chest pain.

Data on animal toxicity to these three types of oils are more extensive. However, again the literature is heavily weighted towards descriptions of aerosol and dermal, rather than oral exposure to oil. Appendix 2 contains the results of aerosol and dermal studies conducted on animals. These studies indicate that both aromatic and non-aromatic oils can be harmful to animals either when they ingest it through their lungs, or when it is applied to their skin. The data suggests that hemorrhagic lungs and various blood ailments are the cause of illness (and sometimes death) in animals exposed to aerosols containing aromatic oils. Exposure to non-aromatic aerosols, on the other hand, usually results in oil accumulations in the lungs. The differential response to the two types of oil mirrors that described earlier on human toxicity to aromatic and non-aromatic containing aerosols.

The data on dermal exposure of animals to oils is also similar to that on humans. The effects of exposing animals to aromatic-containing oils (e.g., hair loss, blood abnormalities, severe skin ailments) appears to be generally more severe than to oils containing no aromatic hydrocarbons. In the latter case, only minor skin irritations developed.

Animal studies conducted on oral ingestion of oil are perhaps more pertinent when assessing the hazards of oil-tainted ground

water. This is because it is by this means of exposure that oily ground water poses its chief potential threat. Table 3 in Appendix 2 summarizes available data on the toxic effects of orally administered oil to test animals. Again, the data seems to suggest that both aromatic and non-aromatic oils can be harmful to terrestrial organisms. However, unlike the data on aerosol and dermal toxicity, the studies on ingestion of aromatic and non-aromatic oils do not lend themselves easily to comparison. This is because the types of animals tested and the oil dosages administered are less similar for the aromatic and non-aromatic oils than is the case with the aerosol and dermal studies. Also, there are fewer studies on oral toxicity from which to make generalizations. However, the data in Table 3 are useful for the purposes of this document because they illustrate that oral ingestion of oil can pose serious health hazards to terrestrial organisms.

3. Drinking Water

Aside from the toxic effects that oil can have on consumers of oil-tainted ground water, the contamination of drinking water with oil is also of great concern because of oil's organoleptic properties.

The previous discussion described, in qualitative terms, the toxic effects of oil to humans and other terrestrial organisms. No quantitative toxicity value for oil was provided because oil's toxicity varies with its chemical composition. Quantitative values have been reported, however, for the concentration at which oil renders water objectionable to drink.

Human taste is very sensitive to oil and, depending on the individual, a concentration between 0.005 and 0.5 pounds in 100,000 gallons of water will produce water which will be described as having a bad taste.³⁶ Oil also has a strong odor which, for many people, makes oil-contaminated water unpleasant to drink. For these reasons, mismanaged waste oil poses a significant potential threat to ground water supplies of drinking water.

Ground water is, of course, an essential environmental resource; at least half the population of the United States depends on it for their drinking water.³⁷ Congress expressed special concern for protection of ground water in the legislative history of RCRA. The Agency views the potential contamination of large portions of ground water as posing a "substantial" hazard to human health and the environment, within the meaning of Section 3004 of RCRA, even if the contamination results not in a direct threat to human health, but rather to the destruction of ground-water resources.

It has been suggested that because petroleum is organoleptically objectionable at very low concentrations, it is unlikely that oil-polluted drinking water will pose a toxic threat to humans. This, however, has never been scientifically determined to be true. Nonetheless, regardless of whether oil produces an adverse organoleptic or toxic threat to consumers of ground water, either threat is significant and detrimental to humans.

B. Hazards posed by mismanagement

As stated earlier, there are three principal sources of unused waste oil: spills, vessel operations, and inadequate storage and formulation. This section explains why unused waste oil derived from spills poses a significant threat to human health and the environment, while that derived from the other two sources poses a minimal threat.

Existing regulations and management practices ensure that waste oil derived from vessel operations does not pose a sufficient environmental threat to warrant its listing as a hazardous waste under RCRA. The first section of this document described how unused waste oil brought ashore* from vessels is normally processed at oil refineries. In the case of oily wastewaters (e.g., ballast water), the wastewater is stored in tanks for a short time until it is released to a refinery's wastewater treatment system.** In the case of oil separated from wastewater (e.g., tank-cleaning water) on board a vessel, the oil is typically used as a feedstock at oil refineries when brought ashore. Thus, in both cases, the unused waste oil is managed in a manner which maximizes its recovery.

Additionally, EPA believes that economic considerations will minimize the threat of improper management of waste oil resulting from inadequate storage and formulation. Because oil

* Unused waste oil discharged to surface water is subject to regulations administered by the Coast Guard (33 CFR Part 157).

** These treatment systems are designed to recover oil from various wastewater streams.

is becoming progressively more expensive, the Agency believes that less and less waste oil will be generated from poor handling practices (e.g., letting oil exceed its shelf life) other than spills. That is, as the cost of oil rises, handling practices should improve. For this same reason, the Agency believes that negligible quantities of waste oil will be generated when unused oil flunks certain specifications. Off-spec oil will either be reblended to meet specifications, or will be used for lower quality uses.* Thus, because the quantity of unused oil that becomes a waste due to inadequate handling or formulation practices is small, the environmental threat posed by this oil should also be small.

Unused waste oil derived from spills does, however, pose a potential significant threat to the environment.** The following discussion will focus on the environmental hazards posed by (1) oil spilled to land, and (2) oily debris generated from cleaning-up spills to land and surface water.

As indicated earlier, the aromatic component of oil is toxic, and contains several substances (including three carcinogens) listed in Appendix VIII of Part 261. If unused oil is spilled or otherwise improperly managed on land overlying an aquifer, its aromatic component may migrate to ground water. The degree

* E.g., 'off-spec' oil destined for use in military vehicles could be sold to retail stores as low cost motor oil.

** Oil spilled to surface water in sufficient quantities to create a sheen has been shown to be harmful to the environment. While in the water, such oil is subject to regulations (40 CFR Part 110) pursuant to Section 311 of the CWA and, thus, no further regulatory control under RCRA is warranted.

to which oil and its components are transferred to ground water is governed by several processes which include:

1. the extraction of soluble components from the oil into residual water in the soil;
2. the transport of dissolved components to the ground-water body, for example by rain water; and
3. the adsorption of oil components on the soil.

The influence of each of these processes depends on the amount and composition of the oil, on the nature of the soil, on the rate of rainfall, and on the ground-water level and its grade.³⁸ Figures 1 and 2 illustrate the effect of several of these factors on oil migration to ground water.³⁹ As can be seen, oil released into soil tends to flow downward, with some lateral spreading. As oil moves down through the soil, some of its components become trapped between individual soil particles and remain behind the main body of oil. Other components continue to travel through the soil, and may eventually reach ground water.⁴⁰

In order to study the behavior of oil spilled to land, soil core samples were taken at the sites of several known oil spills in Alberta, Canada.⁴¹ In general, the total concentration of oil declined with depth, with the total concentration of the aromatic fraction appearing to increase relative to the other two fractions (i.e., naphthenic and paraffinic). Oil was detected in the ground water below several of these sites. These findings are significant for two reasons. First, they document that oil can migrate to ground water. Second, they lend support to the commonly held,

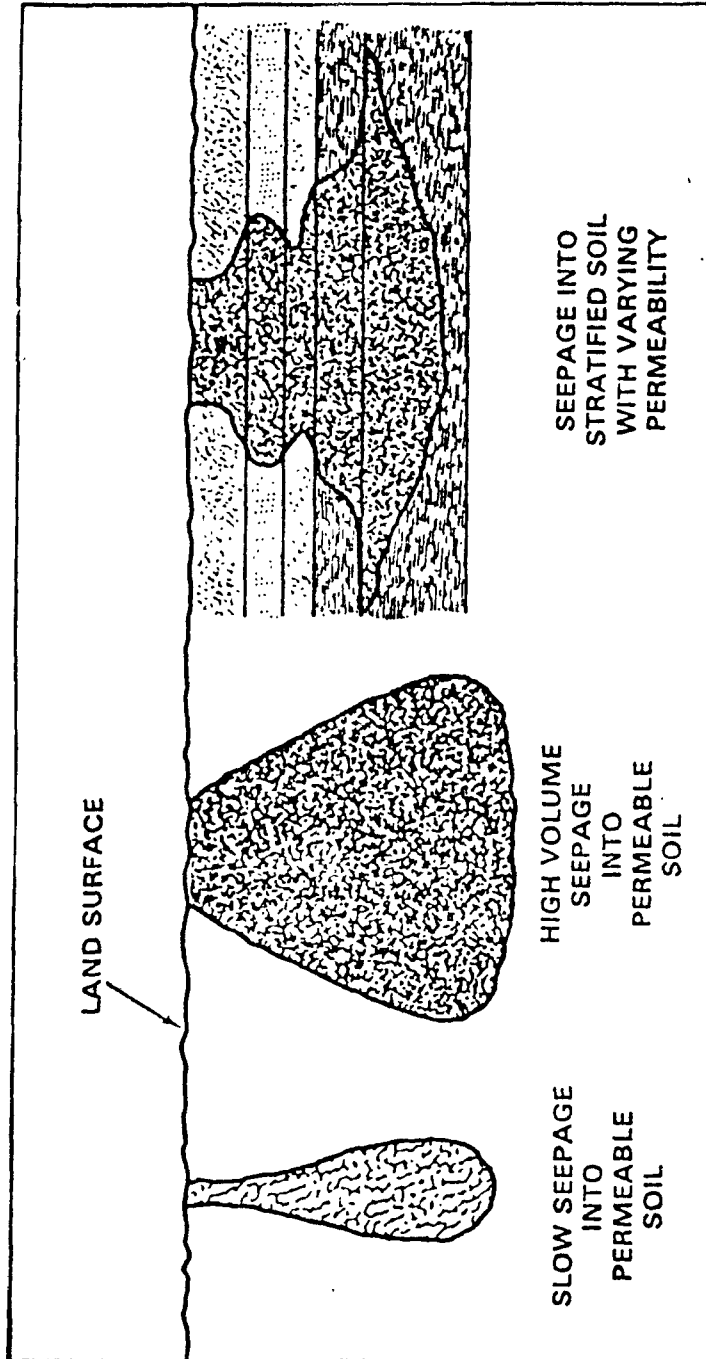


Figure 1 - Oil Seepage

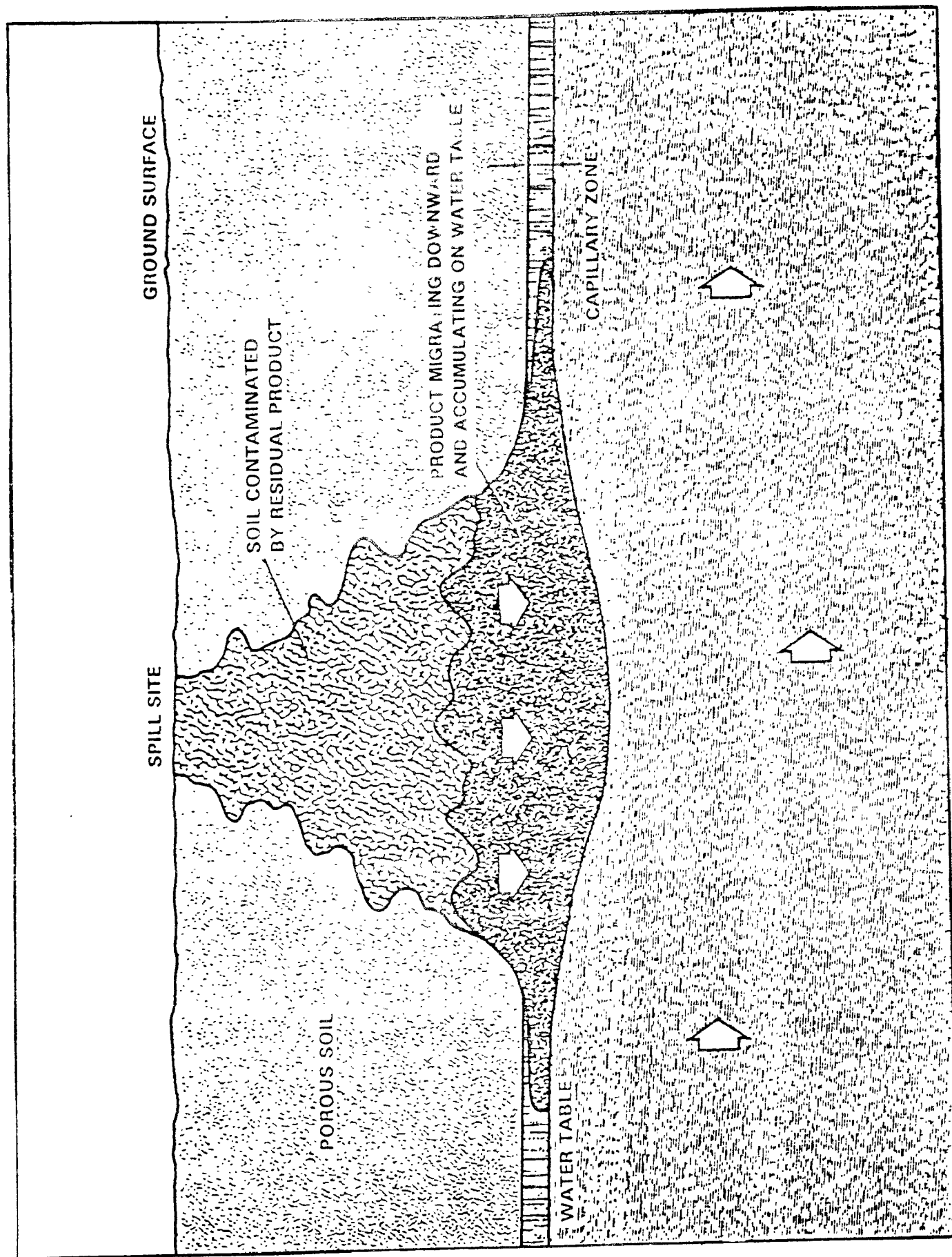


Figure 2 - Typical Behavior in Porous Soil Following a Sudden, High Volume Spill

theory that oil traveling through soil becomes enriched in aromatic hydrocarbons relative to the source of the oil spill.

Contamination of ground water supplies by oil has been reported in all Canadian provinces, in the United States, and in Europe.⁴² In 1968, for example, a major ground water resource in southern California was contaminated with hundreds of thousands of gallons of gasoline.*⁴³

In addition to oil spills, another significant potential source of ground-water contamination is oily debris generated from cleaning-up oil spills to land or surface water. Oily debris is typically disposed of at landfills, landfarms, or incinerators. The facilities used to manage this debris are not always adequate for this purpose. In at least one instance, oil spill debris has been washed from a landfill by floodwaters simply because the disposal site was located in a known floodplain.⁴⁴ In another case, oil was detected in soil samples 7 meters (20 feet) below a landfarm disposing of oily debris. Oil was also found in the ground water below the site.⁴⁵

Oil that has either migrated through soil or has reached ground water is subject only to anaerobic degradation. It has been estimated that anaerobic degradation of oil takes on the order of 100 years.^{46,47} Thus, damage to water resources from oil can be very long-lived.

* Gasoline meets the definition of petroleum-derived oil described earlier and, thus, would be considered to be a waste oil when spilled.

Summary

Oil spilled to land, and oily debris generated from cleaning-up spills to land or surface water, pose a significant threat to ground water supplies. Substantial quantities of both of these types of unused waste oils are generated each year. Past management practices suggest a risk of improper management. The oils have been known to enter ground water when improperly managed. The aromatic component of these oils is not only the most likely to migrate to ground water, but also is the most toxic. Oil is organoleptically objectionable to humans at very low concentrations. Oil that reaches ground water does not readily degrade.

The Agency believes that all of these considerations support the proposed listing as a hazardous waste of (1) oil spilled to land, and (2) oily debris generated from cleaning-up spills to land or surface water. The exception to this is unused waste oil that has essentially no aromatic hydrocarbons (i.e., white oils). Because these oils are used for medicinal purposes, and are allowed to be used in food, the Agency believes it would be inappropriate to list either of the above two types of unused waste oils as hazardous wastes if their petroleum base is white oil.

USED OIL

Used oil is generally categorized as automotive, industrial, or aviation oil.* Used oil is similar to unused oil in that it contains an oil component that poses a potential threat to human health and the environment when improperly managed. Thus, for the same reasons given earlier for unused oil, the Agency believes that used oil should be listed as a toxic (T) hazardous waste. In addition, many used oils contain contaminants which cause them to be hazardous for reasons other than their oil component. The identification of these contaminants and the additional hazards posed by them are the focus of this chapter.

The first part of this chapter describes the quantities generated, typical hazardous contaminants, and the practices commonly used to manage used automotive and industrial oils. This is followed by the Agency's rationale for listing used automotive and industrial oils as hazardous wastes.

I. Constituents and Management Practices

A. Automotive

The Bureau of the Census' most recent (1977) compilation provides the following breakdown of U.S. sales of lubricating oil:⁴⁸

* Used aviation oils are not addressed in this document for two reasons. First, aviation oils make up less than one percent of total oil sales and, thus, relatively little used oil is generated from this source compared to automotive and industrial oils. Second, because of centralized servicing areas, most used aviation oils are collected, segregated, and treated, or -- in the case of synthetic jet fuels -- returned to the manufacturer for reclaiming. The Agency believes that because relatively little used aviation oil is generated, and because that which is generated is usually managed in an environmentally sound manner, it is not imperative that this oil be subject to the hazardous waste management rules at this time.

	<u>Billion of gallons</u>
automotive	1.29
aviation	.02
industrial	
lube	1.03
other	<u>.53</u>
	2.86

According to this source, automotive lube oil sales made up about 45% of the total market in 1977. The Bureau of Census includes the following types of oils in the automotive lube oil category: engine oil, gear lubes, hydraulic oils, and transmission fluids.

1. Constituents

At present, additives comprise greater than 15% by volume of automotive oils.⁴⁹ Table 10 presents the chemical composition and functions of these additives. During service, the additives are chemically changed or consumed, and the oil itself becomes contaminated from both internal* or external** sources.⁵⁰

Table 11 is a comparison of the properties and components of used automotive oils with that of various virgin oils. The table is divided by dotted lines into 3 sections. The first section presents some of the physical properties and chemical components of used automotive oils. The second section shows other physical and chemical properties and components which reflect the additive

* The primary source of internal contamination is breakdown of the additive package and subsequent interaction among its chemical components. These components may be oxidized during combustion, forming corrosive acids.

** Examples of external sources of contamination include soot and lead compounds from engine blowby, dirt and dust; engine wear metal particles; rust; gasoline from incomplete combustion; coolant from imperfect engine seals; water from blowby vapor.

TABLE 10

Lube Oil Additives, Automotive and Industrial Oil

ADDITIVE	FUNCTION
Antiwear/Extreme Pressure Zinc Dithiophosphate Organic phosphates Organic sulfur & chlorine compounds Lead compounds Amines	Forms protective film, reduces wear
Corrosion & Rust Inhibitors Zinc dithiophosphates Basic sulfates Metal phenolates Fatty acids and amines Alkenyl-succinic acids	Prevents corrosion by forming protective film or by neutralizing acids
Detergents/Dispersants Barium, calcium & mag- nesium phenolates Organic phosphates & sulfates Polymeric alkyl thio- phosphates Alkyl succinimides	Disperses insoluble con- taminants by keeping them suspended in the oil
Friction Modifiers Fatty acids and amines Lard oil Organic phosphorous Phosphoric acid esters Molybdenum disulfide	Used in automatic trans- missions and limited slip differentials
Antioxidants Zinc dithiophosphate Aromatic amines Hindered and sulfurized phenols Nitrogen & sulfur compounds	Reduces foam in crankcase
Metal Deactivators Weak organic acids Organic complexes of amines, sulfides, phosphates	Reduces oxidation and pre- vents rust and corrosion by forming a protective film on metal surfaces

TABLE 10 (Cont'd)

Lube Oil Additives, Automotive and Industrial Oils

ADDITIVE	FUNCTION
Pour Point Depressants Polymethacrylates Alkylated naphthalenes Chlorinated paraffins Phenolic polymers	Lowers freezing point, thus allowing free flow at low temperatures
Viscosity Index Improvers Methacrylate polymers Butadiene Olefins Alkylated styrene	Minimizes viscosity changes as temperature fluctuates
Emulsifiers (industrial lubes only) Sulfonates Surfactants Naphthenates Fatty acid soaps	Holds oil-water mixtures in suspension
Biocides/Fungicides (industrial lubes only)	Kills bacteria and fungus which cause odor problems

* Sources: References 55; 49, Table 2-2;
and 51, Table 2.

TABLE 11

Properties and Components of Used Automotive Oil
Compared with Selected Virgin Oils

Property/Component	Used Automotive Oil - Range	Virgin Distillate Range	Virgin Residual Range
Bottom Settlings & Water (BS&W) %	0 - 22	0 - 1.5	0 - 3
Water %	.2 - 33.8 **	0	0
Fuel Dilution %	.4 - 9.7 **	0	0
Flash Point °F	175 - 415	126 - 204	150 - 270
Chlorine ppm	1700 - 4700***		
Br ppm	1000 - 3000 ***		
- - - - -			
Carbon Residue %	1.82 - 4.43**		
Ash %	.03 - 3.78	.002 - .005	0 - .5
N ppm	530 - 1770**		
S ppm	2100 - 6500**	200 - 5900	3000 - 4000
- - - - -			
Ba ppm	10 - 2000		0
Ca	700 - 3000		.7 - 95
Mg	10 - 1108		.4 - 27.9
Na	16 - 300		.1 - 480
P	500 - 2000		0
Zn	300 - 3000		0
Al	.0 - 800		.5 - 219
Cr	8 - 50		13 - 14
Cu	5 - 348		.5
Fe	50 - 2000		10.5 - 230
K	5 - 79		0
Mn	5 - 10		0
Ni	3 - 30		3 - 118
Pb	800 - 11,200		1.7 - 4.1
Si	10 - 875		8.2 - 164
Sn	5 - 112		0
Cd	4		0

NOTE: The term "distillate" in column 3 refers to middle distillate oils (e.g. Nos. 1 and 2 fuel oils); the term "residual" in column 4 refers to heavier fuel oils (e.g., Nos. 4 and 5 fuel oils).

* Source: Unless otherwise indicated,
data are taken from reference 134.

** Data from reference 53, Tables 2, 3, and 4.

*** Data from reference 49, Table 3.

content of the oils. The third section shows the metal content of the oils; the first six elements (Ba, Ca, Mg, Na, P, and Zn) are associated with additive compounds; the remainder are wear and contaminant metals. This table offers an overall picture of the make-up of used automotive oil, and highlights the general differences between these and virgin oils. The remainder of this discussion will focus on the specific toxic components of used automotive oil which provide support (in addition to that provided for unused oil) for its listing as a hazardous waste.

Polynuclear aromatic hydrocarbons (PNA's or PAH's):

As stated above in the discussion of unused oil, PNA's as a class are toxic, and many are potent carcinogens as well. Already found in virgin oils, PNA's are "known to concentrate in used automotive lubricating oils, apparently coming from the gasoline or diesel fuel and their combustion products."⁵¹ The National Bureau of Standards (NBS) uses benzo(a)pyrene (BaP), as an indicator of total PNA content. According to NBS analyses as summarized in a RECON report,⁵² the BaP levels in used motor oils may be as much as 900 times greater than those found in unused motor oil basestocks (see Table 12)*. In absolute terms, a 1975 BERC (Bartlesville Thermal Research Center) analysis of ten used automotive oils found the concentration ranges for three specific PNA's to be: phenanthrene 40-110 ppm; pyrene 30-100 ppm; and 1,2-benzanthracene 3-30 ppm.⁵³

* Note, however, that the BaP content of used diesel oil is less than .15ug/g. This is considerably lower than the levels measured in used gas engine oils.

TABLE 12

Benzo(a)pyrene Concentrations as
Measure of PNA Content in Used and Virgin Oils

<u>Oil</u>	<u>BaP in ug/g</u>
#2 virgin (distillate)	.03 - .6
#6 virgin (residual)	2.9 - 44
virgin motor oil basestocks	.03 - .28
used motor & waste oils	3.2 - 28
used diesel motor oil	< .15
used industrial oil	5.9

Source: reference 50, Table 14.

Trace metals:

Trace metals of concern in used automotive oil derive from several different sources. The extremely high lead content (800-11,200 ppm; see Table 11) is attributed chiefly to piston blowby in engines using leaded gasoline*. Lead compounds may also be a minor component of some antiwear/extreme pressure additives (see Table 10).

Barium, which like lead is absent from automotive lube oil stocks, is generally found in used automotive oil in the range of 10-2000 ppm (see Table 11)**. Barium derives from detergent/dispersant additives (see Table 10), which make up 6.8% by volume of SE quality multigrade motor oil.⁵⁵

According to Table 11, the chromium concentration of used automotive oil ranges from 8 to 50 ppm; cadmium was measured at 4 ppm. The presence of both these trace metals in used automotive oil derives from engine wear.

Nitrosamines:

Nitrosamines are formed when secondary amines react with the following nitrogen compounds: nitrites, nitrates, and nitrogen oxides. A report to the National Science Foundation indicates that, since both nitrogen and amine compounds are found in used automotive oils, the formation of nitrosamines is possible.⁵⁶ Furthermore, various nitrosamines have been patented for use as anti-oxidants in fuels and as a lube

* However, because diesel fuel is unleaded, the lead content of used diesel lube oil is negligible.

** NBS analyses have reported barium levels as high as 3906 ppm in some crankcase oils.⁵⁴

oil additive.⁵⁷ Other precursors to nitrosamine formation are currently used as lube oil additives. These include various aryl and alkyl amines which serve as anti-oxidants, and morpholine which is a corrosion inhibitor.⁵⁸ These "precursors" react with nitrogen compounds in the used oil, in the environment, or in the human body, to form nitrosamines.⁵⁹

Chlorinated hydrocarbons*:

Petroleum is composed of a mixture of hydrocarbons, including benzene and naphthalene. When these and other hydrocarbons are exposed to the significant levels of halogens introduced during automotive use (see chlorine and bromine concentrations, Table 11), halogenated hydrocarbons (e.g., chlorinated benzene and chlorinated naphthalene) may be formed. The halogen content of used automotive oil derives from two sources: additive package breakdown (see Table 10); and addition of chlorine and bromine, as lead scavengers, to leaded gas.

* Until the early 1970's, small amounts of polychlorinated biphenyls (PCB) were added to certain automobile transmission fluids to enhance controlled swelling of rubber seals. Transmission fluids from older automobiles thus may be a source of low level PCB contamination of some used automotive oils.⁶⁰ EPA's regulations under the Toxic Substances Control Act (TSCA) presume that all used oil is contaminated with PCBs.⁶¹ Although information from an independent testing laboratory specializing in used automotive oil analysis indicates that used automotive oil samples are, for the most part, free of PCB contamination, the common collection practice is to mix used oils taken from various sources.⁶² In this way, used automotive oil may be contaminated through contact with PCB-laden hydraulic or transformer oil collected from industrial sources (see section on industrial oils).

2. Management Practices

In 1978, an estimated 50-65% of the motor oil sold for passenger car use was sold to people who change their own oil.⁶³ These people are known in the industry as "do-it-yourselfers" (DIYs). Within the next 5 years, this group is expected to comprise 75-80% of such sales.⁶⁴ Currently, most used oil generated from DIYs (over 200 million gallons) is dumped on the ground or into streams or sewers, or is placed in containers and put out for trash collection.^{65,66}

Service stations and automobile dealerships collect waste oil on their premises in 500-1000 gallon tanks*. The oil collected at service stations is derived from both on-site maintenance of automobiles and DIYs who bring their used oil to these stations. No attempt is made at either service stations or automobile dealerships to segregate used oil from engines using unleaded fuel from that of engines using leaded gasoline.

Used oil tanks at service stations and automobile dealerships are emptied by independent collectors. The collector's trucks generally hold between 2000-6000 gallons. Used oil from several service stations or dealerships is usually placed in the same truck. The collectors normally sell the oil for use as a fuel, a dust control agent, a pesticide/ herbicide carrier, or as a

* In addition to used oil, brake and transmission fluids, gasoline, kerosene, antifreeze (ethylene glycol), and such solvents as benzene, trichlorethane, and perchloroethylene are often placed in used oil tanks at service stations and automobile dealerships. The low flash points, toxicity, and possible carcinogenicity of many of these substances further increase the hazards posed by the used oil.

feedstock to rerefiners.* Other uses which claim small amounts of used oil are asphalt mixes, and use as a herbicide.

Used lube oil from diesel engines generated by large commercial trucking fleets may remain segregated from other used automotive oil in the collection process. Much of this oil goes to rerefiners, with the exception of that produced by the mining and construction industry (about 20% of all diesel vehicles). The practice in these industries is to change the oil in the field, where it is simply dumped on the ground.⁶⁷ Some trucking fleets also mix low levels (2-6.5%) of used diesel lube oil with diesel fuel and burn the resulting blend in their engines.⁶⁸

B. Industrial

The Bureau of Census data cited earlier (see page 43) indicate that industrial oil sales made up about 55% of the total lube oil market in 1977. The industrial category is subdivided into two groups: lube oil, including metalworking oils and oil used in railroad and marine diesel engines; and non-lube oils, including hydraulic, transformer, turbine, and quenching oils.^{69,70}

In general, industrial oils contain an additive package similar to that of automotive oil (see Table 10). Table 13 shows some of the physical properties and chemical components of used industrial oils. Table 12 compares the PNA level of used industrial oil to that of various other used and virgin oils.

* Some collectors treat the oil before selling it, to remove water and solids, and small amounts of oxidation products. Although such "reclaiming" before sale and reuse may produce a cleaner and more marketable oil, the properties and components of concern discussed in this document are not removed or mitigated.

TABLE 13

Properties and Components of Used Industrial Oil

<u>Property/Component</u>	<u>Range</u>	<u>Mean</u>	<u>Maximum</u>
Water %	25.7 - 26.2		
Flash Point °F	315 - 355		
Cl ppm	1000 - 8300		
S ppm	5400 - 10,030		
Pb ppm		125	2000
Ba ppm		59.7	550
Cr ppm		7.9	45
Cd ppm		2.7	21

Source for data on first four properties/components:
reference 51, Table 3.

Source for data on last four components:
reference 141, Table 3-7.

The data contained in these tables must be treated, however, as only a rough sketch of the contaminants that may be found in used industrial oils. The used industrial oil category is much more diverse than that of used automotive oil because industrial oils perform a wider variety of functions compared to automotive oils. The contaminants in industrial oils vary with each function*, as does the type of additive package used. The components of these additive packages are less predictable than those in automotive oils because users of industrial oils frequently have their additive packages custom-blended for their particular needs. Thus, unlike used automotive oil, it is impossible to identify a set of contaminants that can be expected to be present in used industrial oil per se.

The Agency has limited data on contaminants found in some of the larger sub-categories of used industrial oil. This data will be presented next, along with a description of how these types of industrial oil are currently being disposed of or reused. The section is divided into two parts: lube and non-lube oils.

1. Lube Oils

Metalworking oils:

Metalworking oils are lube oils used for cutting, grinding, drilling, and machining metals. They range from 100% oil (neat oil) to low concentrations of oil in water emulsions (soluble oils).

* E.g., the trace metals in used metalworking oils vary with the type of metal that is being cut, ground, drilled, etc.

a. Constituents:

Chlorinated hydrocarbons*:

The chlorine content of used metalworking oils is high, which can lead to significant chlorinated hydrocarbon emissions when the oil is burned. In the neat metalworking oils, the chlorine is derived from the additive package. Metalworking oils require enhanced extreme pressure additives which may contain as much as 18% active chlorine.⁷³

Used soluble metalworking oils are also likely to have a high chlorine content. When the oil is recovered from the oil-water emulsion, the recovery process typically includes breaking the emulsion with hydrochloric acid. Chlorine from the acid may react with the oil's hydrocarbons to form chlorohydrocarbons.

Nitrosamines:

Recent studies indicate that "soluble cutting oils may contain nitrosamines, either as contaminants in amines, or as products from reactions between amines and nitrites".⁷⁴ The nitrosamine content of metalworking oils is attributed to the additive package, specifically to the antiwear/extreme pressure, corrosion and rust inhibitors; friction modifiers; antioxidants; and metal deactivator additives (see Table 10).

* PCBs can enter metalworking oil through "tramp oil" accumulations. Tramp oil is oil (usually hydraulic oil) from other parts of the machine which leaks or drips into metalworking oil. Hydraulic oil is likely to be contaminated with PCBs (as explained later in the discussion on hydraulic oil), and it can accumulate in metalworking oil in sufficient amounts to raise a 5% oil/water emulsion to 10% oil.⁷¹ In addition, PCB additives were used in industrial lube oils prior to 1973.⁷² These could still be contributing to the PCB contamination of used metalworking oils.

Use of synthetic lubricants* in metalworking oils is increasing,⁷⁷ and concentrations of nitrosamines in synthetic cutting oils have been measured at 1-1000 ppm.⁷⁸

Trace metals:

Used metalworking oils are heavily contaminated by fine wear-metal particles (see Table 13), and with barium from detergent/dispersant additives.

b. Management Practices:

Over 64 million gallons of metalworking oils were sold in 1978.⁷⁹ Because the typical metalworking operation does not consume oil, about 60 million gallons of used oil are generated and must be disposed of or reused annually.

The neat oils have an extremely high metal content, the soluble oils have a high water content -- both pose problems for rerefining. The high chlorine and sulfur content of the neat oils, and of the acidified and recovered soluble oils, makes burning undesirable. As a result, only a small amount of these oils -- about 20% or 12.8 million gallons -- is being collected for reuse.⁸⁰ The remainder, is being disposed of by dumping, uncontrolled burning, or by land application.

* Defined as a product made by chemically reacting lower molecular weight materials to produce a fluid of higher molecular weight with planned and predictable properties.⁷⁵ The principle types are esters, silicones, fluoro- and chlorocarbons, and polyoxyalkanes. In 1980, synthetics made up 2% of the total lube (automotive and industrial) market. This figure may be up to 10% by 1985.⁷⁶

Railroad and marine oils:

a. Constituents:

Because railroad and marine use of engine lube oils parallels that of automotive applications,⁸¹ the trace metal content of used railroad and marine diesel engine lube oils should be similar to that of used automotive oil (see Table 11), with the exception of lead. Diesel fuel is unleaded, so there should be little or no lead in any used diesel engine lube oil.

The additive package required by railroads consists of detergents, 10.5% by volume.⁸² This may result in significant barium concentrations in used railroad diesel engine lube oil (see Table 10).

Marine diesel engine lube oils* also require an alkaline detergent additive, up to 15% by volume in the crankcase oils. This too may lead to high barium levels in used marine oil (see Table 10).

b. Management Practices:

About 80% of railroad oil is consumed in use, leaving about 10.3 million gallons to be disposed of or reused. The vast majority (greater than 95%) of this amount is collected, rerefined, and returned to the railroads for reuse.⁸³ Like automotive diesel fleets, the railroads also mix their used lube oil with virgin diesel fuel, at very low blend ratios.

In 1978, about 35.5 million gallons of marine cylinder and crankcase lube oils were sold. Much of the cylinder oil is con-

* All information on marine oils is taken from reference 55, pp. 48-52.

sumed in use; the remainder is drained out of the engine into the bilge tank. Crankcase oil, when changed, is also placed in the bilge tank. In the past, these bilge oils have been dumped at sea. Now, naval and some commercial shipyards collect these used oils.

About 60% of all marine oils are consumed in use. Of the remainder, 16% is collected for reuse as fuel (marine facilities also blend low levels of used lube oils with virgin diesel fuel) or for rerefining. The remaining twenty-four percent (or 8.5 million gallons) is dumped at sea or on the land.

2. Non-Lube Oils:

Hydraulic oils:

Hydraulic oils are widely used in industry, primarily in die-casting, steel foundry operations, automobile production, and mining.

a. Constituents:

Chlorinated hydrocarbons:

Until 1972, PCB-based hydraulic fluids were commonly used. When manufacture of these fluids was discontinued, it was not recommended that hydraulic systems be drained, flushed, or refilled*. Rather, the public was advised to merely replace these fluids (without PCBs) as leaks and spills occurred. As a result, PCB levels in hydraulic systems range from 60 to 500,000 ppm.⁸⁴

* The extreme complexity of hydraulic systems makes it very difficult to eradicate all PCB contamination from these systems.

Nitrosamines:

Nitrosamine precursors may be present in the form of nitrogen and amine compounds, deriving from the anti-rust, anti-oxidant, and anti-wear additives found in hydraulic oils.⁸⁵

b. Management Practice:

In 1978, 234 million gallons of hydraulic oils were sold. Small quantities of this oil were consumed in use or lost through leakage and spills.

Large industrial facilities recover much of their used hydraulic oil, which may be sold to collectors, burned as a fuel supplement in the plant itself, or used as a dust control agent on plant site roads and parking lots. At construction sites and mining operations, however, hydraulic oils are not recovered. It is estimated that 40% of these hydraulic oils, or about 94 million gallons, are disposed of annually.⁸⁶

Transformer Oil:

a. Constituents:

Chlorinated hydrocarbons:

Transformer oils, used in electrical transformers as a heat transfer medium, are straight mineral oils with no additives.⁸⁷ However, until 1977, PCBs were widely used as a dielectric fluid in transformers and other electrical equipment. These PCBs still remain in many transformer systems, contaminating transformer oil.

The preamble to EPA's PCB regulations states that as many as 38% of the 35 million transformers using mineral oil contain between 50 and 500 ppm PCBs.⁸⁸ An independent testing laboratory estimates that about 50% of all transformer oils show greater than 50 ppm PCB contamination. This occurs because, even if transformers are drained and cleaned out, they have "long memories", and PCBs are likely to remain in the system.⁸⁹

In addition to PCBs, transformer oils have also been found to contain trichlorobenzene, a persistent toxic substance.⁹⁰

b. Management Practice:

About 98 million gallons of transformer oils were sold in 1978. This unusually high figure reflects an increased demand to replace PCB-contaminated oil.

Transformer oils do not make a good rerefinery feedstock because of their low viscosity. EPA's PCB regulations strictly control the disposal and reuse options of PCB-contaminated oils. At present, most used oil collectors are refusing all transformer oil, thus putting the burden of proper disposal on the generators.⁹¹

Turbine oil*:

a. Constituents:

Turbine oils are used in steam, natural gas, or dual cycle turbines that generate electricity or run compressors. The oils require a high temperature oxidation inhibitor, about 2% by volume.

* All information on turbine oils is taken from reference 55, pp. 61-62.

Because ashless additives such as aromatic amines or hindered phenols are preferred, nitrosamine precursors may be present in the turbine oils as a result of the additive package.

b. Management Practice:

Eighty-four million gallons of turbine oil were sold in 1978. Turbine oils may be changed as often as once a year, or may be treated and reused for up to 20 years.

Most turbine oil is used in large industrial plants, which tend to collect their used oil. It is estimated that about 50.4 million gallons of used turbine oil is recovered and either disposed of or reused.

Quenching oil:

a. Constituents:

Quenching oils act as a cooling medium for hot metals. These oils contain numerous additives, including barium sulfonate, zinc compounds, sodium nitrate, and antimony trioxide.⁹²

b. Management Practice:

About 50% of the 7.5 million gallons of quenching oils sold in 1978 were collected from metalworking shops. At shops which place used quenching and metalworking oils in the same container, the quenching oils become tainted with the contaminants found in used metalworking oils.

* * * * *

On the whole, mixing of used industrial oils from different sources does not occur to the extent it does with automotive oils. Many users of industrial oil find it more cost-effective to burn

their used oil as a fuel or otherwise manage it (e.g., by using the oil as a dust suppressant on unpaved roads or parking lots on their property), rather than give or sell it to used oil collectors. This is not to say that mixing of different types of used industrial oils does not occur within industrial plants. For financial and space constraints often operate against providing separate storage facilities for, say, neat metalworking oils and soluble oil-water emulsions.⁹³ Nonetheless, the opportunity to segregate oils with different contaminants is greater when generators reuse their oil on-site rather than give it to used oil collectors.

Some used industrial oil is, however, consigned to used oil collectors. The collectors usually transport different types of used oil in the same compartment of their trucks, so that the various contaminants in the individual waste streams become mixed throughout the composite waste oil.

II. Basis for Listing

A. Adverse effects of contaminants in used oil

This section briefly describes the toxic effects of the various contaminants found in certain used oils*. In addition, for each contaminant, the discussion notes if substances containing these contaminants are subject to controls under regulatory programs other than those concerned with solid waste management.

Polynuclear aromatic hydrocarbons (PNAs):

The toxic and carcinogenic effects of PNAs were described earlier in the chapter on unused oil. SO₂, which is present in the vapor produced when used oil is burned, is considered to have a synergistic effect on PNA-induced carcinogenesis.⁹⁴

Halogenated Hydrocarbons:

1. Polychlorinated biphenyls (PCBs):

a. Health Effects: PCBs have been identified by EPA's Carcinogen Assessment Group as exhibiting substantial evidence of carcinogenicity.⁹⁵ PCBs are also highly toxic. They are absorbed through the lungs, the skin, and the gastrointestinal tract; then are circulated throughout the body in the blood, and are stored in the liver, kidneys, lungs, adrenal glands, brain, heart, and skin.⁹⁶

Yusho disease (human PCB poisoning) affected at least 1000 people who ate rice bran oil contaminated with PCBs. These

* Detailed discussions of the adverse environmental effects of many of these contaminants are contained in the criteria documents prepared under Section 304(a)(1) of the CWA. See 45 FR 79318 (November 28, 1980).

victims also evidenced an abnormally high cancer rate of the stomach and liver. It is estimated that the Yusho victims ingested PCBs at a rate as low as 67 ug/kg of body weight per day for 3 months.⁹⁷

Skin lesions have developed among workers exposed to air containing PCBs at levels as low as .1 mg/m³.⁹⁸

b. Ecological Effects: PCBs are inert and persistent, having a tendency to accumulate in waterways and to bioaccumulate in fish. PCB levels of 1 ppb may adversely affect aquatic insects and crustaceans. Concentrations as low as .1 ppb have been shown to depress photosynthesis in phytoplankton and to retard their rate of cell growth and division.⁹⁹

c. Other Regulations: EPA has designated PCBs as a toxic pollutant and has set effluent standards prohibiting any discharge of PCBs into navigable waters by PCB manufacturers, electrical capacitor manufacturers and electrical transformer manufacturers.

The ambient water criterion for PCBs is .001 ug/l.¹⁰⁰ There are no ambient air quality standards for PCBs. However, disposal of PCB-contaminated wastes is governed under TSCA by 40 CFR Part 761. Wastes (specifically used oil) containing less than 50 ppm PCBs may be rerefined or burned without controls, but may not be used as a road oil, dust suppressant, or sealing and coating agent. Used oil with 50-500 ppm PCBs must be burned in a high-efficiency boiler or approved incinerator, where the destruction efficiency is 99.9%; it may also be disposed of in approved chemical landfills. Used oil with greater than 500 ppm PCBs must be disposed of only by high temperature incineration.

PCBs are listed a hazardous constituent in Appendix VIII, 40 CFR Part 261; thus raising the presumption that any wastes containing these substances are hazardous wastes.

The National Institute of Occupational Health and Safety has determined that levels in the workplace for two types of PCB compounds must not exceed 1 mg/m³ (Arochlor 1242) and .5 mg/m³ (Arochlor 1254).¹⁰¹

2. Other halogenated hydrocarbons:

a. Health Effects: Chlorinated benzenes and chlorinated naphthalenes, among other halogenated hydrocarbons, may be found in used oil. Both of these compounds are toxic when ingested or inhaled. Chlorinated naphthalenes are also toxic when applied to the skin, and may produce skin lesions, as well as acute liver atrophy.¹⁰²

These compounds emit toxic fumes when heated to decomposition; they may react with oxidizing materials.¹⁰³

Nitrosamines:

a. Health Effects: Nitrosamines are suspected human, and known animal carcinogens. Evidence of a causal relationship of nitrosamines to human cancer is supported by the following facts: all mammals studied are susceptible to carcinoma induction by at least one nitrosamine; nitrosamines are effective carcinogens by inhalation, ingestion, and dermal contact; nitrosamines can be formed in vivo in mammals through the interaction of nitrosamine precursors, (specifically, injected secondary amines and nitrites).¹⁰⁴

Nitrosamines are carcinogenic and mutagenic in a wide range of animal species, with tumors affecting all vital organs.

b. Ecological Effects*: Plants are capable of assimilating nitrosamines and their precursor compounds from the soil and from water cultures, and can form nitrosamines by metabolic activity. The presence of nitrosamines in plants appears to have no detrimental effect on the plant itself, but may pose a hazard to animals ingesting these plants.

c. Other Regulations: Nitrosamines and their precursors are widely distributed in the environment. Currently available data do not provide sufficient information to estimate total or relative human exposure via ingestion or inhalation, nor are they sufficient to set criteria for maximum exposure. However, nitrosamines are listed as hazardous constituents in Appendix VIII, 40 CFR Part 261, thus raising the presumption that any waste containing these substances is hazardous.

As to nitrosamine precursors, the national primary drinking water standard (NPDWS) for nitrate nitrogen is 10 mg/l.¹⁰⁶ The national primary ambient air quality standard for nitrogen dioxide is 100 ug/m³ (.05 ppm), annual arithmetic mean.¹⁰⁷

Trace Metals

1. Lead:

a. Health Effects: When ingested or inhaled, lead and its compounds are highly toxic.¹⁰⁸ Lead is a cumulative poison, and can attack the liver and kidneys, the brain and nervous system, as well as the blood vessels and other tissues. Lead poisoning can be fatal.

* Information on the ecological effects of nitrosamines is taken from reference 105.

It is believed that the human intake rate at which lead accumulation begins to exceed excretion is about 1 mg/day.¹⁰⁹ However, chronic ingestion of .1 mg/day over several years has been reported to cause lead poisoning.

b. Ecological Effects: Lead is rarely taken up by plant roots, but can contaminate vegetation exposed to airborne particles of the metal. If such plants are used for forage or fodder, their lead content may enter the food chain.¹¹⁰ Lead has also been shown to be toxic to aquatic organisms, with the degree of toxicity depending on such variables as water temperature and alkalinity.¹¹¹

c. Other Regulations: EPA has set .05 mg/l as the NPDWS for lead. 5 mg/l (or 100 times the NPDWS) is the threshold concentration for lead, above which the extract from any lead-containing waste meets the characteristic of "EP Toxicity" pursuant to 40 CFR Part 261.

The ambient air quality standard for lead is 1.5 ug/m³, averaged over 3 months. The OSHA standard is 50 ug/m³, based on an 8-hour workday.¹¹²

2. Barium

a. Health Effects: Ingestion of soluble barium compounds results in severe gastrointestinal distress and muscular paralysis. Inhalation of barium compounds can lead to baritosis, a benign respiratory affliction.¹¹³

Fatalities from inhalation of barium oxide,¹¹⁴ and from ingestion of barium carbonate¹¹⁵ have occurred. The fatal dose of barium for humans is reported to be 550-600 mg.¹¹⁶

b. Ecological Effects: The existence of soluble barium compounds toxic to aquatic species is unlikely under normal marine and freshwater conditions.¹¹⁷

c. Other Regulations: The NPDWS for barium is 1 mg/l. 100 mg/l is the threshold concentration for barium, above which the extract from any barium-containing waste meets the characteristic of "EP Toxicity" under 40 CFR Part 261.

The OSHA criterion for soluble barium compounds is .5 mg/m³.

3. Chromium*

a. Health Effects: Hexavalent chromium compounds are highly toxic when ingested, inhaled, or applied to the skin.¹¹⁸ Controlled experiments with animals indicate that hexavalent chromium compounds are toxic and possibly fatal to animals, with the skin, mucosa, lungs, and kidneys being affected.¹¹⁹ Chromium is also a suspected cause of lung cancer.¹²⁰

b. Ecological Effects:

Low levels of hexavalent chromium (.03-64 ppm) inhibit algae growth. Significant adverse effects on fish have been observed at .2 mg/l of hexavalent chromium.¹²¹

Chromium is taken up through plant roots. Although natural soil contains some chromium (40 ppm, mean), additions of even small amounts (5-50 ppm) have been shown to damage vegetation.¹²²

c. Other Regulations: The NPDWS for chromium is .05 mg/l. The waste extract concentration for chromium triggering the

* When incinerated, chromium oxidizes to hexavalent chromium, thus rendering potentially hazardous all chromium-containing wastes that are burned.

"EP Toxicity" characteristic for hazardous wastes under 40 CFR Part 261 is 5 mg/l*.

OSHA standards are 1 mg/m³ for the metal and its insoluble salts, and .5 mg/m³ for its soluble chromium salts.

4. Cadmium

a. Health Effects: Cadmium compounds are extremely toxic and may be fatal when ingested or inhaled.¹²³ When ingested, little absorption is likely to occur because of rapid elimination by vomiting. When inhaled, cadmium accumulates in the kidneys, liver, pancreas, and thyroid, and is retained in the body for many years.¹²⁴

The estimated fatal dose of inhaled cadmium to humans is about 50 mg/m³ for one hour.¹²⁵

b. Ecological Effects: Cadmium is taken up from the soil by plant roots. If present in the air as a dust contaminant, it can also enter plants via precipitation.¹²⁶ Such cadmium uptake can result in decreased crop yields.¹²⁷ Furthermore, foods grown in cadmium-contaminated soils irrigated with cadmium-polluted water can accumulate sufficient quantities of the metal to pose a human health hazard.¹²⁸

Cadmium levels of less than 1 ug/l can have adverse effects on certain fish species.¹²⁹

c. Other Regulations: The NPDWS for cadmium is .01 mg/l. The waste extract concentration for cadmium triggering the

* On October 30, 1980, EPA proposed to amend the "EP toxicity" characteristic for chromium to apply to hexavalent chromium instead of total chromium. (see 45 FR 72029-34).

"EP Toxicity" characteristic for hazardous wastes under 40 CFR Part 261 is 1 mg/l. Application of wastes containing cadmium to food chain crops is controlled under 40 CFR 257.3-5 and 40 CFR 265.276.

OSHA sets its cadmium standard at 2 mg/m³.

B. Hazards posed by mismanagement

Accurate data on the quantity of used oil generated and the management practices currently used to reuse or dispose of it are difficult to obtain because there are so many sources of used oil and no national reporting requirements for the oil's generation or management. Estimates vary considerably as to how much used oil is generated each year, with a recent EPA draft report placing the amount at 464 million gallons for used automotive oils and 380 million gallons for used industrial oils.¹³⁰

The four most frequently cited methods for managing used oil are: burning it as a fuel; applying it to road surfaces or other land areas as a dust suppressant or road oil; re-refining it to produce lube oil basestocks; and disposing of it either in landfills or by indiscriminately dumping it into sewers or on the ground. Again, there is considerable disagreement in the literature as to how much oil is managed by each of these methods. The following breakdown (by percentage) is consistent with most reports on this subject:

Burned as a fuel	55%
Used as a road oil, dust suppressant or other land application use	15%
Re-refined to a lube oil basestock	10%
Disposed of in landfills, or indiscriminately dumped	20%

There are potential hazards associated with many of these management practices.

Land application:

When used oil is applied to the land (either as a road oil, dust suppressant, or when indiscriminately dumped), the oil and its contaminants can migrate by flotation (precipitation-induced runoff), by percolation through the soil, by direct runoff (if the application is excessive), by volatilization, and by dust transport.¹³¹ The quantities of oil and contaminants transported by these various mechanisms varies greatly, depending on terrain, soil porosity, wind and rain conditions, temperature, traffic volume, and rate of application. Nonetheless, the potential for environmental contamination is significant.

The chapter on unused oil described the hazards posed when oil migrates to surface water and ground water. Trace metals in used oil may also pose a threat to human health and the environment because they may be taken up by plant roots from oil-contaminated soil. Volatilization of the oiled surface can produce toxic metal-laden dust particles, which can enter vegetation via precipitation.¹³² Such dust can also coat vegetation, which may be used as food for wild or domestic animals. Thus, toxic metals in used oil may enter the food chain.

The toxic effects of other used oil contaminants (specifically halogenated hydrocarbons, including PCBs, and nitrosoamines) were described in the previous section of this document. These contaminants may migrate to surface and ground waters if used oils containing them are improperly applied to land surfaces.

Landfilling:

When used oil is disposed of in an insecure landfill, the potential for contamination of ground water supplies is the same as that described earlier for unused oil. The potential harm is of course greater for used oil than with unused oil because the former contains hazardous contaminants which may migrate to ground water along with the oil component.

Burning:

When used oil is burned, either as a fuel or for the purpose of thermal disposal, its contaminants may enter the atmosphere.

Anywhere from 20 to 100% of the lead in used oil entering a steam boiler can be expected to be emitted from the stack. Most of the remainder is deposited on tubes and elsewhere in the combustion furnace. Furnace deposits may be emitted during soot-blowing, where this is practiced, or they may eventually be removed during furnace and boiler cleaning.¹³³

Seventy-six to 79% of the lead and 3 to 51% of the barium in used oil burned as fuel are emitted in particles less than a micron in size.¹³⁴ These submicron size emissions remain suspended in the atmosphere longer and, therefore, may have a wider dispersion range than larger particles.¹³⁵ Compared to large particles, submicron-size particles tend to penetrate more deeply into the respiratory tract, and are retained there longer.¹³⁶

Other trace metals in used oil may be expected to behave similarly to lead with regard to stack emissions, but very limited data are available.

Stack burning tests measuring PNA emissions from boilers burning used oil indicate that PNA emissions are similar to those resulting from burning virgin oils.¹³⁷

Damage Cases

Used oil serving as a mask for dangerous substances has been implicated in a number of damage incidents, as have many of the contaminants discussed above.* These incidents show empirically the potential for substantial harm if used oil is managed improperly.

In Missouri in 1971, about 5000 gallons of waste oil containing 300 ppm dioxin were sprayed on the floor of a horse arena. Sixty-three horses died; many other horses, dogs, cats and birds became ill after exposure to the arena. One child who played in the area developed epistaxis, gastrointestinal disorders, and severe hemorrhagic cystitis. Ten other persons were afflicted with diarrhea, headaches, nausea, and persistent skin lesions.

In Nebraska in 1958, an explosion attributed to burning used oil with a low flash point (possibly resulting from gasoline dilution) occurred in a meat packing plant. As a consequence, the State enacted legislation establishing a minimum flash point for used oil burned as a fuel.¹³⁹

In 1978, 33,000 gallons of transformer oil contaminated with PCBs were dumped along 210 miles of secondary roads in North Carolina. The North Carolina Agriculture Commissioner cautioned against any direct or indirect human consumption of crops grown within 100 yards of the spill. Nearby residents reported nausea, dizziness and cramps.¹⁴⁰

In Texas in 1978, used oil serving as a "mask" for toxic wastes was applied to roads as a dust suppressant. Nearby residents suffered headaches and nausea; livestock died. The used oil was found to contain nitrobenzene and cyanide.

* Unless otherwise indicated, all information on damage cases is taken from reference 138. Many other damage incidents from improper management of used oil are contained in EPA's collection of incidents from individual states.

Summary

When used oil is improperly managed, its oil component poses the same potential threat to ground and surface waters as does that of unused oil. In addition to the arguments made earlier for listing certain waste unused oils as hazardous wastes, the Agency believes that the following points lend further support for deeming some used oils to be hazardous wastes:

1. Most used automotive oils, and certain industrial oils, have been shown to contain significant concentrations of some or all of the following contaminants:

- a. polynuclear aromatic hydrocarbons such as benzo(a)-pyrene, phenanthrene, and 1,2-benzanthracene, which are potent carcinogens;
- b. polychlorinated biphenyls (PCB's), which are carcinogenic, and other halogenated hydrocarbons, which are persistent toxics;
- c. nitrosamines, or their precursors, which are potent carcinogens;
- d. trace metals, such as lead, barium, chromium, and cadmium, which are toxic as elements and in compounds.*

2. Typical used oil storage, collection and transportation practices often result in related wastes, such as anti-freeze and solvents, being mixed in with used oil. Furthermore, used oil is sometimes deliberately contaminated, thus serving as a "mask" for such toxic substances as dioxin, nitrobenzene, and cyanide.

3. Over 800 million gallons of used oil are generated in the United States each year.

* The levels of these metals in used automotive oils, other than used diesel lube oil, exceed that which triggers the "EP toxicity" characteristic for hazardous waste under 40 CFR Part 261 (see Table 11). Used diesel oil contains negligible quantities of lead and, thus, would meet the characteristic of "EP toxicity" for only barium, chromium, and cadmium.

In Kansas, 56 cattle died and 112 more had to be slaughtered when used oil laden with PCBs was used on back-rubbers on a farm.

In Minnesota, used oil, grease, various other hydrocarbons, and phenols were disposed of in an unlined basin. Soil and ground water were found to be contaminated with PNAs up to 1400 feet from the basin.

In Massachusetts, one million gallons of solvents, used oil, toxic metals, and halogenated hydrocarbons leached from an abandoned disposal site. Rainwater runoff resulted in contamination of the Concord River's aquatic environment.

4. Used oil applied to the land (e.g., as a road oil, dust suppressant, or when indiscriminately dumped) poses an environmental hazard resulting from the direct release of the oil onto the land, and through percolation and run-off into ground and surface waters.

5. Used oil disposed of in insecure landfills may also leach through the bottom of such landfills, and subsequently contaminate ground water supplies.

6. Because of the presence of contaminants, uncontrolled burning of certain used oils, either as a fuel or for the purpose of thermal disposal, may result in significant levels of hazardous emissions to the environment. This, in turn, may expose humans, wildlife, and vegetation in the area to these harmful substances.

7. Many of the contaminants in used oil are persistent, bioaccumulative, or have potential for increased penetration of the respiratory tract, thus magnifying the possibility of exposure and harm.

8. Improper management of waste oil has caused many actual damage incidents.

The Agency believes that all of these considerations support the listing of used automotive and industrial oils as toxic (T) hazardous wastes.

Used automotive oils will be listed as hazardous wastes based on the following constituents : polynuclear aromatic hydrocarbons (including benzo(a)pyrene and benz(a)anthracene); chlorinated naphthalene; chlorinated benzenes; nitrosamines; lead; barium; chromium and cadmium. Though certain types of used automotive oils may not contain one or more of these substances (e.g., used diesel lube oil does not contain lead), the fact that different types of automotive oils are typically stored and transported in the same container argues for the Agency's presumption that most used automotive oil will eventually become contaminated with most of the hazardous substances specified above.

Significant quantities of used industrial oils are source-segregated and managed on-site (e.g., burned as a fuel, used as a dust suppressant). Therefore, unlike used automotive oils, it would be inappropriate to generalize that all industrial oils will eventually become contaminated with hazardous substances found in individual types of used oils. For this reason, a common set of contaminants has not been specified as the basis for listing used industrial oil per se as a hazardous waste.

Instead, all used industrial oil will be listed as a hazardous waste based on its aromatic oil component*. This is the same as was done for unused oil. In addition, where the Agency has sufficient data on the hazardous contaminants of particular types of industrial oils, these substances will be listed as additional reasons for deeming the oil to be hazardous. For now, the following types of used industrial oils will be deemed to be hazardous wastes based on the following hazardous constituents in addition to aromatic hydrocarbons:

Metalworking: nitrosamines; barium

Railroad and marine: barium

Hydraulic: PCBs**; nitrosamines

Transformer: PCBs

Turbine: nitrosamines

* The exception to this are used industrial oils that have no aromatic oil component (e.g., finishing oils made with white oil basestocks).

** Even though used oils containing greater than 50 ppm PCBs are deemed to be hazardous wastes under RCRA, EPA intends to subject these oils to the management standards under TSCA (40 CFR Part 761) rather than RCRA.

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APPENDIX 1

AFFADAVIT SUPPORTING EPA'S "SHEEN TEST"

AFFIDAVIT

DISTRICT OF

COLUMBIA

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KENNETH BIGLANE, being duly sworn, deposes and says:

I am the Director of the Division of Oil and Special Materials Control, Office of Water Program Operations, of the United States Environmental Protection Agency. It is my official duty to formulate and to direct national programs to respond to discharges of oil and hazardous materials and to prevent such discharges, pursuant to section 311 of the Federal Water Pollution Control Act, as amended, P.L. 92-500, 86 Stat., 816 et seq., 33 USC 1251 (FWPCA). I held the position equivalent to my present one within the Federal Water Pollution Control Administration of the Department of the Interior when the regulations concerning discharges of oil, now codified at 40 CFR 110, were originally promulgated in September 1970 (Appendix I).

I hold a Bachelor of Science degree and a Master of Science degree in Zoology from Louisiana State University. My graduate studies were in fisheries physiology, parasitology, histology, and fish toxicology.

From 1952 to 1956, I served as an Aquatic biologist with the Louisiana Wildlife and Fisheries Commission. Louisiana then had approximately 20,000 oil and gas wells, and during that period I investigated and assessed the environmental impact of several hundred oil spills ranging in size from amounts barely sufficient to cause a sheen on the surface of the water to those of thousands of barrels. During this same period, I conducted a study of the environmental effects of oil and oil field brines which included field observations, chemical and biological laboratory analyses, and toxicity bioassays.

From 1956 to 1962, I served as both the Chief of the Division of Water Pollution Control of the Wildlife and Fisheries Commission and as Executive Secretary of the Louisiana Stream Control Commission. My experience with oil pollution during this period included administering the State investigative and regulatory program which included the production, refining, and transportation of petroleum products.

During the period 1962 to 1966, I served as Headquarters Biologist and Operations Officer of the United States Public Health Service in Washington, D. C., and in 1966 I began service with the Federal Water Pollution Control Administration of the

Department of the Interior. As a part of my duties with the Federal Water Pollution Control Administration and subsequently with the U.S. Environmental Protection Agency (EPA), I personally investigated and evaluated more than 20 oil discharges, some examples are shown in Appendix 2(a). These field investigations of oil discharges included: evaluation and survey of biological effects of oil discharges, review of methods and procedures employed in the oil removal operations and countermeasures to mitigate damage to the environment, and critique of oil spill response contingency planning including, organizational structure and notification and coordination of Federal, State and local authorities.

In addition to the personal field investigations previously noted, I have, in my capacity as Director of the Oil and Special Materials Control Division, participated in a supervisory and advisory capacity with respect to thousands of oil spills nationally and internationally. My activities included advice on countermeasures and oil spill clean-up methods and procedures for minute spills in environmentally sensitive locations and large spills in similar areas, including the open sea.

In addition to my experience in the field and national program office supervision and guidance, I have participated in numerous international activities related to biological effects of oil in the environment and oil spill contingency planning, prevention and control. I served as a U.S. representative to the International Conference on Oil Pollution of the Sea, Rome, Italy, October 1968.

Upon my return from this Conference, I once again visited the beaches and coasts of Brittany and Cornwall to re-evaluate the effects of cleanup efforts and the environmental impact of the Torrey Canyon oil spill of 1967.

I served as a U.S. Delegate to the International Conference on Marine Pollution Damage, Brussels, 1969. The results of this Conference produced two Conventions (1) the International Convention Relating to Intervention on the High Seas in Cases of Oil Pollution Damage; and (2) the International Convention on Civil Liability for Oil Pollution Damage.

In June 1971, I was invited by the Australian Government to testify and gave extensive testimony at Brisbane, Australia, before the Royal Commission on the Great Barrier Reef with respect to the environmental impact of offshore oil drilling and production operations.

In December 1971, I received the EPA Gold Medal for Exceptional Service for activities "in developing a national program responsive to the need for controlling spills of oil and hazardous materials."

I was a member of an Interagency Task Force chaired by the Department of State to develop the Great Lakes Water Quality Agreement with the Canadian Government which was jointly signed on April 15, 1972. This International Agreement, which includes oil pollution standards for the Great Lakes, marked the first time two Heads of State committed their Governments to cooperate in the cleanup and preservation of such a large, shared natural resource.

I served as a consultant to the Smithsonian Institute with respect to coastal zone oil pollution in Indonesia and attended a symposium hosted by the Indonesian Government in Jakarta, Indonesia, in August 1973.

Since 1968, I have also served as a member of the United States National Committee on Prevention of Marine Pollution which advises The United States Department of State in the formulation of U.S. Policy on international oil pollution.

I have published articles in scientific and other journals and have presented papers before technical and other groups. A list of over 30 such articles, ranging from aquatic biology and the environmental effects of oil and other pollutants to oil spill prevention and regulation, is attached as Appendix 2(b).

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Section 311(b)(3) of the FWPCA prohibits discharges of oil in harmful quantities. 40 CFR Section 110 defines "harmful quantity of oil" as a quantity sufficient to "cause a film or sheen upon or discoloration of the surface of the water or adjoining shorelines or cause a sludge or emulsion to be deposited beneath the surface of the water or upon adjoining shorelines."

Each year the U.S. Coast Guard and EPA receive notification, pursuant to the reporting requirements of Section 311(b)(5) of the FWPCA, of approximately 10,000 spills of oil into or upon the navigable waters of the United States. The number of unreported spills of oil is not known, but I believe that the number of oil spills

occurring annually substantially exceeds 10,000. Eighty percent of the reported spills are of 10 barrels or less (one barrel is 42 gallons at 60 degrees Fahrenheit). Such smaller spills have a seriously degrading effect on the environment. This is particularly true of spills occurring on inland waters, in estuarine areas, and near the coastline, which generally are habitats for birds and other wildlife. Estuarine and coastline areas are the productive zones for sea life, and are particularly important and sensitive to oil discharges.

A recent report, The Appearance and Visibility of Thin Oil Films on Water (EPA-R2-72-039)(Appendix 3) prepared by EPA's Edison Water Quality Research Laboratory, demonstrates that there is a quantitative relationship between the appearance of an oily layer on water and its thickness. This report states that an oily layer of at least approximately 150 nanometers (nm) thick (1 nanometer = 1 billionth of a meter or 39.37 billionths of an inch is required in order to produce a sheen as defined in 40 CFR 110. Specific colors in an oily layer denote specific thicknesses in the range of 300 - 900 nm. With thicknesses greater than 900 nm, colors become dull and grade into light and dark bands with little color. These inherent appearances of oil were found to be a function of thickness and not a function of oil type or of water type. The results of this study are confirmed by the study of the American Petroleum Institute and the General Research Corporation.

This same report (Appendix 3) demonstrates a direct correlation between thickness of an oily layer measured in nanometers and surface concentration measured in milligrams per square meter. Thus, for example, an oily layer of 150 nanometers thickness, which would produce a sheen as defined in 40 CFR 110, contains a surface concentration of 150 milligrams per square meter.

Surface concentration may be mathematically converted to concentration in the water column for any given depth to which the oil could be mixed. If an oily layer of 150 nanometers were to be mixed into the top 1 centimeter of water, the resultant concentration would be 15 parts per million (ppm):

$$\frac{150 \text{ mg}}{10^4} \times \frac{10^3 \text{ cc}}{\text{liter}} = 150 \times 10^{-1} \frac{\text{mg}}{\text{liter}} = 15 \text{ mg/liter or } 15 \text{ ppm}$$

If the same amount of oil were mixed into the upper 10 centimeters of water, the resultant concentration would be 1.5 ppm.

Although surface concentration can be mathematically converted into concentrations in the water column, the physical and chemical properties of oil make uniform distribution extremely unlikely. Oil is a complex mixture of various components with differing physical and chemical properties. All oil discharges contain components which float on the surface and components which dissolve in the water. Depending upon factors such as the wave action, the amount of suspended solids in the receiving waters and the weather, floating oily layers may also result in oily water emulsions and oily sludge. Since oil discharges may produce these various conditions in the aquatic environment, the harmful effects of oil in the water cannot be measured by

reference to concentrations of dissolved oil components alone.

The harmful effects of floating oil, oily emulsions and oily sludge are widespread, obvious, and long-term.

The attached Appendix 4(a) is an annotated bibliography, prepared under my direction, of scientific works documenting some aspects of the ecological damage that is caused by floating oily layers. The devastating damage caused to waterfowl by floating oil needs no documentation. In the presence of an oil film, ducks are imperiled when swimming or diving for food. As a result of the loss of insulating ability of feathers contaminated by oil, oil soaked ducks cannot maintain a normal body temperature and die from exposure. The viability of duck eggs becomes greatly reduced as a result of contamination from oil-soaked plumage. While preening to cleanse their feathers of oil, waterfowl ingest oil and, as a result, become susceptible to pneumonia and gastro-intestinal irritation. Amounts as small as a one-inch circle on the belly of one species of waterfowl (murre) is sufficient to destroy the insulating air pocket and cause death from exposure.

The scientific publications in Appendix 4(b) also show that small amounts of crude oil have damaging effects on other organisms as well: reproduction in marsh grasses is inhibited, chemoreception of fish larvae is blocked, susceptibility of seagrass to parasites is increased, mangrove seedlings are killed, herring larvae develop abnormally.

Appendix 5 is a report summarizing recent research carried out by an interdisciplinary team of scientists under the direction of Dr. L. R. Brown of Mississippi State University to determine the environmental effects of crude oil in Gulf Coast estuaries. Dr. Brown is a Professor of Microbiology and Associate Dean of the College of Arts and Sciences of Mississippi State University. He holds B. S., M. S., and Ph. D. degrees in Bacteriology from Louisiana State University. He has published more than 50 articles in scientific journals on biological and microbiological topics. Since 1958, he has been engaged in petroleum related microbiology. Examination of the interim results of this ongoing research reveals the following salient points as submitted by Dr. Brown:

- "1. The sensitivity of selected estuarine organisms to oil pollution varies between organisms and with time of year.
- "2. Exposure of shrimp, Penaeus sp., to as little as 0.1 ml of oil in 130 liters of water will elicit anomalous behavior. A 2 ppm oil in water mixture results in demonstrable oil uptake and 15 ppm is sufficient to produce a total kill in most instances.
- "3. While mullet, Mugil cephalus, and oysters, Crassostrea virginica, can withstand the addition of a large volume of oil applied at one time, fatalities are noted when small (calculated to produce a 1 ppm mixture of oil in water), intermittent

applications are used. Exposure to a single application (producing a 75 ppm oil in water mixture) causes significant alterations in the normal metabolic processes of these organisms.

"4. The addition of 1.5 liters of crude oil per square meter causes a significant decrease in marsh productivity.

"5. Additions to experimental aquariums of emulsified crude oil calculated to produce concentrations of 0.5-6.0 ppm but analyzed to be 0.25-3.0 ppm are sufficient to kill 50 percent of the copepods [microscopic animals important in the fish food chain], Acartia sp., present.

"6. Oysters exposed to a 300 ppm mixture of crude oil in water for 96 hours still demonstrate an "oily" taste after 3 months in clean water."

Also attached as Appendix 6, is a copy of an extract from the Report of the National Technical Advisory Committee on Water Quality Criteria, dated April 1, 1968 (U.S. Government Printing Office). This appendix contains a list of the scientists who prepared the Report. The Report shows scientific evidence of the harmful effects of floating oily layers, oily emulsions, and oily sludge on fresh water organisms; marine and estuarine organisms; and wildlife such as waterbirds, muskrats and otters.

The Committee recommended that, to protect marine life, oil should not be deposited into estuarine or coastal waters in sufficient quantities (1) to be detected as a visible film or sheen, or by odor; (2) to cause tainting of fish and/or edible invertebrates; (3) to form an oil-sludge deposit on the shores or bottom of the receiving water; or (4) to become effective toxicants according to the criteria recommended in the "Toxicity" section of the Report.

The environmental damage caused by discharges of oil in quantities sufficient to produce a sheen on the surface of the water has been widely recognized. Moreover, effective enforcement of any oil spill proscription requires that the spill of a prohibited quantity be readily determinable. Under the "sheen" provision of 40 CFR 110, it is a simple matter for a responsible person to know which spills are prohibited. On the other hand, a spill limitation based on quantities measured by volume (e.g., quarts, gallons, barrels) or weight (e.g., lbs.), would be virtually impossible to enforce. First, only the spiller has any possible way of determining the quantity of the spill. Second, it has been my experience in investigating oil spills that persons at the scene and responsible for the spill are frequently unaware of how much oil has been discharged and its effect on the environment, even within very broad limits. As a result, the "sheen" test is well suited to define a discharge which damages the environment and to provide a regulatory mechanism which will work. This combination of environmental harm and enforcement workability has led other nations and international organizations to adopt a visible oil standard to abate oil pollution.

Recent amendments of the 1954 International Convention for the Prevention of the Pollution of the Sea by Oil, to which more than 70 nations were parties, confirmed the 1954 Convention's permission of vessel ballast discharges which "would produce no visible traces of oil on the surface of the water." This same standard was adopted by Congress in the Oil Pollution Act Amendments of 1973 designed to implement the Convention.

The Agreement between Canada and the United States of America on Great Lakes Water Quality, signed by the President and Prime Minister Trudeau at Ottawa on April 15, 1972, defined "harmful quantity of oil" to mean:

"any quantity of oil that, if discharged into receiving waters, would produce a film or sheen upon, or discoloration of, the surface of the water or adjoining shoreline or that would cause a sludge or emulsion to be deposited beneath the surface of the water or upon the adjoining shoreline"

This definition of "harmful quantity of oil" is identical to the definition at issue in this proceeding.

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Section 311(b)(4) of the FWPCA provides that a quantity of oil which:

"at such times, locations, circumstances, and conditions, will be harmful to the public health or welfare of the United States, including, but not limited to, fish, shellfish, wildlife, and public and private property, shorelines, and beaches except that in the case of the discharge of oil into or upon the waters of the contiguous zone, only those discharges which threaten the fishery resources of the contiguous zone or threaten to pollute or contribute to the pollution of the territory or the territorial sea of the United States may be determined to be harmful."

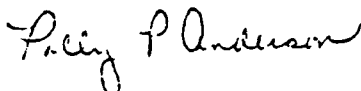
Based on the foregoing and my experience in evaluating the environmental effects of oil spills, it is my opinion that an oil spill sufficient to produce a film or sheen on the surface of the water is large enough to cause harm to the environment.

Subscribed and sworn to before me,
A Notary Public, in and for the
District of Columbia, This
3rd day of May, 1974.


KENNETH BIGLANE

My Commission expires November 30, 1976

POLLY P. ANDERSON



ONLY APPENDICES 4 THROUGH 6 OF THE AFFADAVIT ARE PRESENTED IN THIS DOCUMENT BECAUSE THE AFFADAVIT'S OTHER APPENDICES DO NOT DEAL DIRECTLY WITH OIL'S TOXIC EFFECTS ON AQUATIC ORGANISMS.

APPENDIX 4 a

DOCUMENTED HARMFUL EFFECTS OF SMALL QUANTITIES OF CRUDE OIL ON LIVING ORGANISMS

1. Baker, J. M. 1971. Seasonal effects. In The Ecological Effects of Oil Pollution on Littoral Communities, Ed. Cowell, E. B. Institute of Petroleum, London.

Oiling of marsh plants during the early stages of flowering has drastic effects as a result of damage to buds or primordia. Oiling of open flowers frustrates the formation of seed.

2. Blumer, M. 1973. Interaction between marine organisms and oil pollution. Environmental Protection Agency Report number EPA-R3-73-042, May 1973.

Hydrocarbons are remarkably stable in marine sediments and in the fatty tissues of marine organisms. Even chemically reactive hydrocarbons can move unaltered through several levels in the marine food web.

3. FWQA - 1969. Report of the National Technical Advisory Subcommittee on Water Quality Criteria for Fish and Other Aquatic Life and Wildlife.

British investigators have attributed the disappearance of eel grass (Zostera sp.) to minute quantities of oil. Oil weakens the plant and makes it susceptible to attack by the parasitic protozoa Labyrinthula.

4. Gardner, G. R. 1972. Chemically induced lesions in estuarine or marine teleosts (fish). Proceedings, Symposium on Fish Pathology, Armed Forces Institute of Pathology, Washington, D. C.

Deterioration of the chemoreceptor structures of (silverside fish) Menidia menidia was found after exposure to both soluble and insoluble components of Texas-Louisiana crude oil for 168 hours.

5. Glynn, P. W. et al. 1971. Fundamental analysis for determining the effects of oil pollution on the ecology of a tropical shore. Report, Smithsonian Tropical Research Institute.

Mangrove communities are highly sensitive to crude oil contamination. Major elements of the fauna have not returned after 33 months.

6. Keinhold, W. W. 1970. The influence of crude oils on fish fry. FAO Technical Conference on Marine Pollution, Dec. 9-18, 1970, Rome, Italy. 10 pp.

Toxic components are dissolved from oil films injuring herring larvae and younger stages of floating eggs. Herring larvae were unable to avoid oil contaminated water because chemoreceptors are blocked very quickly upon contact with oil components.

7. Mackin, J. G. 1950. A comparison of the effects of the application of crude petroleum to marsh plants and to oysters. Texas A&M Research Foundation. As reported in IMCO Study VI, Appendix 3.

Seedlings of the mangrove Avicennia were killed by application of 25 ml of crude oil per square foot of water area.

8. Mironov, O. G. 1967. The effects of low concentrations of oil and petroleum products on the development of eggs of Black Sea turbot. Vop. Ikhtiol. 7: pp 577-580.

Black Sea flatfish larvae were killed by exposure to 100 ppm fresh crude oil in 24 hours. At 0.01 ppm mortality was delayed and 23-40 percent of the larvae developed abnormally.

9. Smith, J. E. ed. 1968. "Torrey Canyon" pollution and marine life. Mar. Biol. Assoc. U.K. Cambridge Univ. Press.

An indirect effect of oil pollution accounted for the death of intertidal crustaceans. As a result of biodegradation of oil, dissolved oxygen was depleted and small crustaceans which had sheltered under stones were suffocated.

10. Tuck, L. M. 1960. The Murres. Dep. Northern and Natl. Resources, Natl. Parks Branch, Canadian Wildlife Service, Ser. 1.

A patch of oil, one inch in diameter, on the belly of a murre (waterfowl) was sufficient to destroy the insulating air pocket and cause death from exposure.

APPENDIX 4 b

DOCUMENTED HARMFUL EFFECTS OF OILY LAYERS, OILY EMULSIONS AND OILY SLUDGES ON LIVING ORGANISMS

a) Effects of free oil on waterfowl

1. Clark, R. "Oil Pollution and the Conservation of Seabirds," International Conference on Oil Pollution of the Sea, Rome (1969), found that oiled bird feathers become matted together destroying the water repellent property and allowing water to replace the air normally trapped in them.

2. Erickson, R. "Oil Pollution and Migratory Birds," Atlantic Naturalist, 18 (1) 5-14, 1963, found that bird plumage becomes oil-soaked and water-logged such that birds lose buoyancy and their ability to fly.

3. Chubb, J. "Observations on Oiled Birds, 1951-53," Northwest Nature, (S.S.) 2: 460-461, 1954, showed that in the presence of an oil film diving ducks were unable to dive for food.

4. Hartung, R. "Energy Metabolism in Oil Covered Ducks," J. Wildlife Management, 31 (4): 798-804, 1967, showed that as a result of the loss of insulating air in the feathers (ref. 1 above) oil-soaked ducks lost more than twice the heat of unsoaked ducks.

5. Tuck, L. "The Murrs," Department of Northern Affairs and Natural Resources, National Parks Branch, Canadian Wildlife Service, Ser. 1, 1960, documented that a patch of oil one inch in diameter is

sufficient to destroy the insulating air pocket and cause death from exposure to the chilling effect of the sea.

6. Hartung, R. and Hunt, G. "Toxicity of Some Oil to Waterfowl," J. Wildlife Management 31 (4) 798-804, 1966, in laboratory experiments found that various industrial oils caused lipid pneumonia, gastro-intestinal irritation, fatty livers and adreno-cortical hyperplasia when fed to ducks in doses which were regarded to be less than that which would be ingested during preening of oil plumages.

7. Hartung, R. "Some Effects of Oiling on Reproduction of Ducks," J. Wildlife Management 29 (4) 872-874, 1965, showed that the viability of embryos is greatly reduced when the eggshell becomes smeared with oil from the contaminated plumage of the female.

8. Rittinghaus. "On the Indirect Distribution of the Oil Pest in a Sea Bird Sanctuary," Onithol Mitteil, 8 (3), 1956, found that oiled tern eggs did not hatch.

b) Effects of free oil on water living organisms

1. McKee and Wolf. Water Quality Criteria: State of California Water Quality Control Board, 2nd Ed., 1963, reported studies showing that free oil may act by direct contact on the epithelial surfaces of fish and interfere with respiration, may coat and destroy algae and other plankton and may interfere with the natural processes of aeration and photosynthesis.

2. Dr. Clarence Tarzwell, Director of the National Marine Water Quality Laboratory, in his testimony before the Senate Subcommittee on

On Oceans and International Environment, 1971, stated that surface oil may blanket the surface of the water and prevent the uptake of oxygen and may act as a contact toxicant for surface organisms or organisms that come to the surface may get it into their gills. He also reported on studies with 300 plankton which showed growth inhibition-resulting from surface oil concentrations of 0.8 gallons per acre-foot of water. Based on studies at the Edison Water Quality Laboratory and by the American Petroleum Institute this represents a quantity of oil causing a rainbow discoloration of the surface of the water and a film only .00008 cm in thickness.

3. Straughan, D. "Oil Pollution and the Environment," 1970 Evangeline Section Regional Meeting of the Society of Petroleum Engineers, 1970, reported barnacles (c. fissus) smothered by free oil.

4. Kenyon (personal communication) found that sheens of surface diesel oil were sufficient to coat the fur of two sea otters and cause death due to exposure in Alaskan environments.

5. Massachusetts Institute of Technology, 1970, Man's Impact on the Global Environment: Report of the Study of Critical Environmental Problems noted that chlorinated hydrocarbons are much more easily dissolved in floating films of oil than in water and can then be carried into the water column upon dispersal of the film. One study was reported which showed the concentration of chlorinated hydrocarbon (DDT) to be 10,000 times higher in an oil film than in the underlying water column.

6. Kunhold, W. "The Influence of Crude Oils on the Fish Fry: FAO," Technical Conference on Marine Pollution, Dec. 9-18,

1970, Rome, Italy, reported that toxic components dissolved from floating oil films injured larvae and young stages of floating eggs.

Likewise harmful effects from emulsified oils are found:

1. Mass. Institute of Technology "Man's Impact on the Global Environment: Report of the Study of Critical Environmental Problems," 1970, stated that toxic effects of emulsified oils to fishes can result from direct contact coating of fins and asphixiation.

2. McKee and Wolf Water Quality Criteria: State of California Water Quality Control Board, 2nd Ed., reported studies indicating that emulsified oils act by direct contact on epithelial surfaces of fish to interfere with respiration and may coat and destroy algae and other plankton.

3. Clendenning, K. and North, W. "Effects of Wastes on the Giant Kelp, Macrocystis pyufere," Waste Disposal in the Marine Environment, Proc. 1st Int. Conf. Pergamon Press, N.Y., 1960, reported that emulsions of diesel oil in sea water caused the death of sea urchins.

4. Tarzwell, C. - testimony referenced above, stated that when emulsified oil gets into the gills of gill-breathing organisms it can be toxic. They can also be ingested directly when the droplets are small. The ingested hydrocarbons in addition to direct toxic effect can be incorporated into the flesh and passed up the food chain similar to the persistent chlorinated hydrocarbons.

Finally, the harmful effects of sludged oils include:

1. Zo Bell, C. "The Occurrence, Effects and Fate of Oil Polluting the Sea," Int. Conf. Water Pollution Research, 1962, oil is readily adsorbed by clay and silt and after burial almost no bacterial decomposition occurs.

2. Blumer, M., Souza, and Sass, J., "Hydrocarbon Pollution of Edible Shellfish by An Oil Spill", Int. Jour. on Life in Oceans Coastal Waters, Vol. 5, No. 3, March 1970, describes widespread and long-term damage to bottom living organisms as a result of persistent sedimented diesel oil resulting from a barge spill.

3. Tarzwell, C. - testimony cited above, states that oil going to the bottom and can blanket the bottom and kill through direct contact. When broken up it can be ingested and passed up the food chain.

4. Erickson, R. "Effects of Oil Pollution and Migratory Birds," Biological Problems in Water Pollution, 3rd Seminar (1962), R. A. Taft San. Eng. Center, Cincinnati, Ohio, 1965, noted that migratory birds are indirectly affected by deposits of oil on the bottom in shallow water or along the shore that reduce the available food supply of both plant and animal matter. Various elements in food chains are eliminated by chemical or physical properties of the oil, or items in the diet of waterfowl may become unavailable by being overlaid or imbedded in tarry materials.

5. Battelle Memorial Institute Oil Spillage Study Literature Search and Critical Evaluation for Selection of Promising Techniques to Control

and Prevent Damage, 1967, points out that the accumulation of petroleum sludge on the bottom may prevent germination and growth of plants and the production of invertebrates important as food, either by smothering or by toxic effects.

6. Water Quality Criteria, National Technical Advisory Committee, 1968, states that settleable oily substances may coat the bottom, destroy benthic organisms, and interfere with spawning areas. Oil may be absorbed quickly by suspended matter, such as clay, and then due to wind action be transported over wide areas and deposited on the bottom far from the source.

7. North, W., et al. "Successive Biological Changes Observed in a Marine Cove Exposed to a Large Spillage of Mineral Oil in Pollutions Marines par les Microorganismes et les Produits Petroliers," Symposium de Monaco, 1964, documented long-term damage to bottom fauna resulting from a spill of crude oil in 1957. Populations of several species had not recovered four years after the incident.

REPORT

to

DIVISION OF OIL AND SPECIAL MATERIALS CONTROL

of the

ENVIRONMENTAL PROTECTION AGENCY

on

EPA Contract No. 68-01-0745

by

Lewis R. Brown
Program Director
Mississippi State University

26 April 1974

Appendix 5

INTRODUCTION

On June 30, 1972, Mississippi State University was awarded a three-year contract by the Environmental Protection Agency to study "The Fate and Effect of Oil in the Aquatic Environment-Gulf Coast Region." This contract (EPA Contract No. 68-01-0745) is an interdisciplinary, multiinstitutional effort involving senior scientists from Mississippi State University, the University of Southern Mississippi and the Gulf Coast Research Laboratory. In addition to being responsible for the microbiological aspects of the program, I serve as the Program Director. The major effort in this program is directed toward investigating the chronic effects of subacute levels of oil on the ecosystem and it should be emphasized that the investigations include not only well replicated laboratory bioassay experiments but also field studies. To date all experiments have been conducted with Empire Mix crude oil and salinities in the range of 12-18 ppt. This report is a synopsis of some of the more salient results to date; specifics can be found in Progress Reports 1-6, the Interim Report and the forthcoming Seventh Quarterly Report.

RESULTS

Crude oil has only limited solubility in water, albeit there are some water soluble components present. The total oil present

in the water column can be increased significantly by emulsification but a majority of the oil will become attached to particulate matter, evaporate and/or rise to the surface. Under these conditions, the use of the phraseology "oil concentration in the water column" is of questionable value in most bioassay tests even for tests of short duration. Uptake of oil by biological specimens is dependent not only upon the concentration of oil in the water and the method of application but also on the total time of exposure and thus to the total amount of oil to which the organism has been exposed. For example, our results have shown that the greater the amount of oil in the water column, the greater the uptake by shrimp when dosages of emulsified oil calculated to yield 2, 4 and 8 ppm oil were added to test aquaria (29 gal) in the laboratory. Significant uptake by the shrimp was demonstrated 12 hours after the addition of oil (the first sampling after the oil was added). It is noteworthy to point out that these data are based on analyses conducted using a liquid chromatographic technique which determines aromatic compounds rather than aliphatic compounds since in many instances gas chromatographic analyses failed to indicate oil uptake. As expected the average oil concentration in dead organisms was considerably greater than in organisms surviving, thus suggesting differences between individual organisms. Another point of considerable significance is the fact that the TL₅₀ value varies seasonally and thus extrapolation from laboratory data to the field must take this factor into account. In the presence of

emulsified oil (15 ppm) the shrimp exhibit a "spiraling phenomenon" which should make them far more susceptible to predation. Upon removal from the oily water, the shrimp revert to normal behavior. Erratic behavior by shrimp has been observed in the laboratory with the addition of as little as 1 drop of oil in a 29 gallon aquarium.

In an experiment involving the spillage of oil into a brackish water pond, it was noted that menhaden which exhibited erratic behavior at the surface were quickly devoured by other fish, once again illustrating the potential problem of oil altering normal behavior patterns required for survival.

Both mullet and oysters can survive high doses (350 ppm or greater) of emulsified oil in short term experiments but significant changes in enzyme levels can be attributed to the presence of oil in tests employing 75 ppm oil added to the system. The true significance of these findings in regard to long term survival, reproduction, etc, are not clear at this time, but suffice to say, exposure to oil does alter the normal metabolic activity of the organisms. In more recent studies it has been found that the addition of small amounts (1 ppm) of oil daily for 11 days, followed by 11 days with no oil additions, 11 more days of oil additions, etc., drastically alters the results. Under these conditions oysters began to die during the second oil addition period and mullet began to die during the third oil addition period. Additional tests are being conducted but the results to date seem to imply that the

sequential addition of oil is far more toxic to mullet and oysters than is the addition of a large amount of oil at one time.

Some histological abnormalities have been found in organisms exposed to oil, but on the basis of the results to date it cannot be said with certainty that they were caused by oil.

There seems to be a lot of controversy over the length of time required for oysters to cleanse themselves of the "oily taste" after exposure to oil. Our studies have shown that after exposure of oysters to 300 ppm emulsified oil (1 dose) for 96 hours, the "oily taste" is still detectable even after 3 months of depuration in clean water. It should be pointed out that the exact length of time for depuration in the environment is dependent upon season, salinity, and other facts.

Crude oil has been shown to cause significant decreases in marsh grass productivity in in situ experiments.

Particularly germane to the present report are the results of recent tests just conducted on Acartia (found in brackish and high salinity water). Cultures obtained from the ecosystem ponds to be employed in the field studies yielded TL_{50} values (96 hr) of 0.5-2.0 ppm (1.25 ppm, average) for emulsified oil; cultures obtained from the Gulf yielded TL_{50} values (96 hr) of 1.0-2.0 ppm (1.50 ppm, average) for the emulsified oil; and laboratory cultures yielded TL_{50} values (96 hr) of 2.0-6.0 ppm (4.0 ppm, average) for the emulsified oil. The TL_{100} values (96 hr) for the above cultures were 6-10 ppm, 6-10 ppm, and 10 ppm respectively.

These values are based on the quantities of oil added to the system and actual analyses of the water revealed oil concentrations of 50% of the values reported above.

SUMMARY

In summation, and within the experimental procedures outlined in the progress reports prepared for this contract, the following points are submitted.

1. The sensitivity of selected estuarine organisms to oil pollution varies between organisms and with time of year.
2. Exposure of shrimp, Penaeus sp., to as little as 0.1 ml of oil in 130 liters of water will elicit anomalous behavior. A 2 ppm oil in water mixture results in demonstrable oil uptake and 15 ppm is sufficient to produce a total kill in most instances.
3. While mullet, Mugil cephalus, and oysters, Crassostrea virginica, can withstand the addition of a large volume of oil applied at one time, fatalities are noted when small (calculated to produce a 1 ppm mixture of oil in water), intermittent applications are used. Exposure to a single application (producing a 75 ppm oil in water mixture) causes significant alterations in the normal metabolic processes of these organisms.

4. The addition of 1.5 liters of crude oil per square meter causes a significant decrease in marsh productivity.
5. Additions to experimental aquariums of emulsified crude oil calculated to produce concentrations of 0.5-6.0 ppm but analyzed to be 0.25-3.0 ppm are sufficient to kill 50 percent of the copepods, Acartia sp., present.
6. Oysters exposed to a 300 ppm mixture of crude oil in water for 96 hours still demonstrate an "oily" taste after 3 months in clean water.

Appendix B

Water Quality Criteria

Report of the
National Technical Advisory Committee
to the
Secretary of the Interior

APRIL 1, 1968
WASHINGTON, D.C.



FEDERAL WATER POLLUTION CONTROL ADMINISTRATION

copy 6

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Fresh Water Organisms

Oil

Oil slicks are barely visible at a concentration of about 25 gal/sq mi (Amer. Petroleum Inst. 1949). At 50 gal/sq mi, an oil film is 3.0×10^{-6} inches thick and is visible as a silvery sheen on the surface. Sources of oil pollution are bilge and ballast waters from ships, oil refinery wastes, industrial plant wastes such as oil, grease, and fats from the lubrication of machinery, reduction works, plants manufacturing hydrogenated glycerides, free fatty acids, and glycerine, rolling mills, county drains, storm-water overflows, gasoline filling stations, and bulk stations.

Wiebe (1935) showed that direct contact by fish (bass and bream) with crude oil resulted in death caused by a film over the gill filaments. He also demonstrated that crude oil contains a water-soluble fraction that is very toxic to fish. Galtsoff, et al. (1935) showed that crude oil contains substances soluble in sea water that produce an anaesthetic effect on the ciliated epithelium of the gills of oysters. Free oil and emulsions may act on the epithelial surfaces of fish gills and interfere with respiration. They may coat and destroy algae and other plankton, thereby removing a source of fish food, and when ingested by fish they may taint their flesh.

Settleable oily substances may coat the bottom, destroy benthic organisms, and interfere with spawning areas. Oil may be absorbed quickly by suspended matter, such as clay, and then due to

wind action or strong currents may be transported over wide areas and deposited on the bottom far from the source. Even when deposited on the bottom, oil continuously yields water-soluble substances that are toxic to aquatic life.

Films of oil on the surface may interfere with reaeration and photosynthesis and prevent the respiration of aquatic insects such as water boatmen, backswimmers, the larvae and adults of many species of aquatic beetles, and some species of aquatic Diptera (flies). These insects surface and carry oxygen bubbles beneath the surface by means of special setae which can be adversely affected by oil. Berry (1951) reported that oil films on the lower Detroit River are a constant threat to waterfowl. Oil is detrimental to waterfowl by destroying the natural buoyancy and insulation of their feathers.

A number of observations made by various authors in this country and abroad record the concentrations of oil in fresh water which are deleterious to different species. For instance, penetration of motor oil into a fresh water reservoir used for holding crayfish in Germany caused the death of about 20,000 animals (Seydell, 1913). It was established experimentally that crayfish weighing from 35 to 38 g die in concentrations of 5 to 50 mg/l within 18 to 60 hours. Tests with two species of fresh water fish, ruff (small European perch), and whitefish (fam. Coregonidae) showed that concentrations of 4 to 16 mg/l are lethal to these species in 18 to 60 hours.

The toxicity of crude oil from various oil fields in Russia varies depending on its chemical composition. The oil used by Veselov (1948) in the studies of the pollution of Belaya River (a tributary in the Kama in European Russia) belongs to a group of methano-aromatic oils with a high content of asphalt, tar compounds, and sulfur. It contains little paraffin and considerable amounts of benzene-ligroin. Small crucian carp (*Carassius carassius*) 7-9 cm long were used as the bioassay test animal. This is considered to be a hardy fish that easily withstands adverse conditions. The water soluble fraction of oil was extracted by shaking 15 ml of oil in 1 liter of water for 15 minutes. The oil film was removed by filtration. Dissolved oxygen was controlled. A total of 154 tests were performed using 242 fishes. The average survival time was 17 days at the concentration of 0.4 ml/l of oil but only 3 days at the concentration of 4 ml/l. Further increase in concentration had no appreciable effect on fish mortality.

Seydell (1913) stated that the toxicity of Russian oil is due to naphthenic acids, small quantities of phenol, and volatile acids (Veselov, 1948).

Cairns (1957) reports the following 96-hour TL_{50} values of naphthenic acid for bluegill sunfish (*Lepomis macrochirus*)—5.6 mg/l; pulmonate snail (*Physa heterostrophia*)—6.1 to 7.5 mg/l (in soft water), and diatom (species not identified)—41.8 to 43.4 mg/l in soft water and 28.2 to 79.8 mg/l in hard water. Naphthenic acid (cyclohexane carboxylic acid) is extracted from petroleum and is used in the manufacture of insecticides, paper, and rubber.

Chipman and Galtsoff (1949) report that crude oil in concentrations as low as 0.3 mg/l is extremely toxic to fresh water fish. Dorris, Gould, and Jenkins (1960) made an intensive study of the toxicity of oil refinery effluents to fathead minnows in Oklahoma. By standard bioassay procedures, they found that mortality varied between 3.1 percent to 21.5 percent after 48 hours of exposure to untreated effluents. They concluded that toxicity rather than oxygen demand is the most important effect of oil refinery effluents on receiving streams.

Pickering and Henderson (1966b) reported the results of acute toxicity studies of several important petrochemicals to fathead minnows, bluegills, goldfish, and guppies in both soft water and hard water. Standard bioassay methods were used. Because several of the compounds tested have low solubility in water, stock solutions were prepared by blending the calculated concentrations into 500 ml of water before addition to the test container. Where necessary, pure oxygen was supplied by bubbling at a slow rate. The petrochemicals tested were benzene, chlorobenzene, O-chlorophenol, 3-chloropropene, O-cresol, cyclohexane, ethyl benzene, isoprene, methyl methacrylate, phenol, O-phthalic anhydride, styrene, toluene, vinyl acetate, and xylene. These petrochemicals are similar in their toxicities to fish, with 96-hour TL_{50} values ranging from 12 to 368 mg/l. Except for isoprene and methyl methacrylate, which are less toxic, values for all four species of fish for the other petrochemicals ranged from 12 to 97 mg/l, a relatively small variation. In general, O-chlorophenol and O-cresol are the most toxic and methyl methacrylate and isoprene are the least toxic.

Recommendation: In view of available data, it is concluded that to provide suitable conditions for aquatic life, oil and petrochemicals should not be added in such quantities to the receiving waters that they will: (1) produce a visible color film on the surface, (2) impart an oily odor to water or an oily taste to fish and edible invertebrates, (3) coat the banks and bottom of the water course or taint any of the associated biota, or (4) become effective toxicants according to the criteria recommended in the "Toxicity" section.

Marine and Estuarine Organisms

Crude oil and petroleum products

The discharge of crude oil and petroleum products into estuarine and coastal waters presents special problems in water pollution abatement. Oils from different sources have highly diverse properties and chemistry. Oils are relatively insoluble in sea and brackish waters and surface action spreads the oil in thin surface films of variable thickness, depending on the amount of oil present. Oil, when adsorbed on clay and other particles suspended in the water, forms large, heavy aggregates that sink to the bottom. Additional complications arise from the formation of emulsions in water, leaching of water soluble fractions, and coating and tainting of sedentary animals, rocks, and tidal flats.

Principal sources of oil pollution are numerous. Listed in order of their destructiveness to ecosystems, they are:

- (1) Sudden and uncontrolled discharge from wells towards the end of drilling operation.
- (2) Escape from wrecked and submerged oil tankers.
- (3) Spillage of oil during loading and unloading operations, leaky barges, and accidents during transport.
- (4) Discharge of oil-contaminated ballast and bilge water into coastal areas and on the high seas.
- (5) Cleaning and flushing of oil tanks at sea. On the average, a ship's content of such wastes is estimated to contain 2 to 3 percent oil in 1,000 to 2,000 tons of waste.
- (6) Spillage from various shore installations, refineries, railroads, city dumps, garages, and various industrial plants.

Spillage From Wrecked Oil Tankers

Even though wrecks of oil tankers along the Atlantic coast and subsequent spillage of oil into the sea have been reported several times, no thor-

ough examination has been made of the effect of oil pollution on local marine life, except for frequent references to the destruction of waterfowl. One of these disasters attracted the general attention of the public and members of the Audubon Society of New England. One night in 1952, two tankers, the *Fort Mercer* and the *Pendleton*, went aground on the shoal of Monomoy Point, Cape Cod. Large amounts of oil spilled from the broken vessels, spread long distances along the shore, and were responsible for high mortality of ducks (scoters and eiders). Many thousands of oil-smeared dying birds were seen along the coast. Attempts to save some of the birds by removing the oil with various solvents failed. No published records are found on the effect of this massive spillage on aquatic life. According to the records of the Massachusetts Audubon Society, serious oil spreads threatening fish and bird life have occurred at least six times since 1923 along the beaches of Cape Cod. The latest occurrence was on Sunday, April 16, 1967. Heavy films of crude oil appeared along the coast from Chatham to Provincetown, Mass. and spread to Cape Cod Bay, Nantucket Island, and Boston. The shores of the National Seashore Park were seriously affected and hundreds of ducks and brant were found dead or dying.

The massive spillage of oil may constitute a disaster of a national and even international magnitude as has been dramatically demonstrated by the wreck in March 1967 of the super tanker *Torrey Canyon* carrying 118,000 tons of crude oil. About one-half of the load gradually spilled near Seven Stones Reef, off the southern coast of England, where the tanker was stranded. By the middle of April, patches of crude oil began to appear on the French coast in Brittany, threatening the productive oyster farms in the inlets and estuaries. It is obvious that a disaster of such magnitude is beyond the scope of an ordinary pollution problem in coastal waters. The probability of a recurrence of heavy oil spillage is, however, very real because of the present trend in the methods of transporting oil in very large and apparently vulnerable tankers. It has been reported that Japan operates a tanker, *Idemitsu Maru*, of 205,000 tons holding capacity. A super tanker of over 300,000 tons capacity is under consideration and a design of a 500,000-ton tanker appeared in the press.

Effect of Oil Spillage on Aquatic Life of a Small Marine Cove

W. J. North, et al. (1965) made a valuable study of the effect of massive spillage of crude oil into a small cove in lower California Bay. Prior to

the spillage, the investigators were engaged in a study of bottom fauna and flora of the cove and were in possession of background information which made it possible for them to record the changes that took place after the water of the cove was contaminated by the 59,000 barrels of oil that escaped from the wreck of the tanker *Tampico* on March 29, 1957. Among the many dead and dying species observed a few weeks after the disaster, the most frequently found were abalones (*Haliotis fulgens*, *H. rufescens*, and especially *H. cracherodii*), lobsters (*Panulirus interruptus*), pismo clams (*Tivela stultorum*), mussels (*Mytilus* sp.), sea urchins (*Strongylocentrotus franciscanus*, *S. purpuratus*), and sea stars (*Pisaster giganteus*, *P. ochraceus*). A slight improvement of the bottom fauna was noticeable a few months after the disaster, but extensive recovery became apparent only 2 years later. Four years after the accident, the populations of abalones and sea urchins still were reduced greatly and seven species of animals previously recorded in the cove had not been found at all.

Combined Effect of Oil and Sewage Pollution

The oil and sewage pollution effects on aquatic organisms of the Novorossiysk Bay (Black Sea, U.S.S.R.) was recently studied by Kalugina, et al. (1967). For a number of years, this bay has been receiving a mixed daily discharge of 15,000 to 30,000 cubic meters of petroleum refinery wastes and domestic sewage. There is marked decrease of various valuable species of mollusks (*Spisula subtruncata*, *Tapes rugatus*, *Pecten ponticus*) and complete destruction of oyster beds (*Osireia taurica*) due to the combined effect of pollution and depredations by a carnivorous gastropod (*Rapana*). Samples were collected 1 to 25 meters from the outfall for bioassay. Copepods (*Acartia clausi*) placed in samples taken 25 meters from the outfall were killed in 24 hours. Larvae of decapods and gastropods in samples taken 10 to 25 meters out perished in 3 to 4 days. *Calanus* was killed in 5 days in samples taken 1 meter out, but survived the 10-day test in the samples taken 5, 10, and 25 meters from the outfall. There also was a noticeable change in the distribution and species composition of benthic algae.

Color of Oil Film on the Surface of Water

The color of the oil film on the water surface is indicative of the thickness of the slick and may be used as an indicator of the volume of oil spilled.

According to data published by the American Petroleum Institute (1949), the first trace of color that may be observed as a surface film on the sea is formed by 100 gallons of oil spread over 1 square mile. Films of much darker colors may indicate 1,332 gallons of oil per square mile. Experiments conducted by the Committee on the Prevention of Pollution of the Seas (1953) showed that 15 tons of oil covered an area of 8 square miles. In 8 days, it had drifted about 20 miles from the point of discharge. The same committee (1953) indicated another source of oil pollution that should not be neglected. It has been found that unburned fuel oil escaping through the funnels of oil-burning ships may comprise 1 to 2 percent of the total oil consumed and it may be deposited on the sea surface. British investigators attributed the disappearance of eel grass (*Zostera*) to minute quantities of oil. Oil weakens the plant and makes it susceptible to attacks of a parasitic protozoan (*Labyrinthula*). Observations made several years ago at Woods Hole showed that young *Zostera* that began to reappear in local bays after several years of absence were already infected by this microorganism even though they appeared to be healthy.

Adsorption of Oil by Sand, Clay, Silt, and Other Suspended Particles

Oil of surface films is easily adsorbed on clay particles and other suspended materials, forming large and relatively heavy aggregates that sink to the bottom. The surface of the water may appear free from pollution, until the sediment is stirred by wave action and the released oil floats up again.

During World War II, a product known as "carbonized sand" was manufactured for the U.S. Navy and used for the primary purpose of rapidly removing oil spilled or leaked from ships. Carbonized sand was used principally as a rapid method to prevent and stop fires. Sand and oil aggregates, being much heavier than sea water, sank very rapidly and remained on the bottom. Experimental work has shown that the toxic effect of oils is not diminished by this method (Chipman and Galtsoff, 1949). Since the end of World War II, a number of preparations to be used as solvents, emulsifiers, and dispersing agents of oil slicks in harbor waters appeared in New Zealand, Western Europe, and the United States. These preparations are being offered under various trade names and their chemical composition is not always stated. It is often claimed that such compounds remove oil slicks more efficiently than mopping with straw or

coarse canvas fabric (skuba), a method extensively used in Auckland Harbor (Chitry, 1948). It is, however, generally recognized that various detergents and emulsifiers are toxic to aquatic life and therefore compound the danger of oil pollution. Mechanical means such as preventing the spread of a slick by surrounding it with floating barriers (plastic blooms), spreading sawdust and removing an oil aggregate by scooping or raking, and erecting grass or straw barriers along the beaches are probably more effective at present than the chemical methods of dispersing or dissolving oil. Even anchoring oil by combining it with relatively heavy carbonized sand seems to be preferable to chemical methods.

Toxicity of Crude Oil and Petroleum Products

Oil may injure aquatic life by direct contact with the organism, by poisoning with various water soluble substances that may be leached from oil, or by emulsions of oil which may smear the gills or be swallowed with water and food. A heavy oil film on the water surface may interfere with the exchange of gases and respiration.

A number of observations have been recorded of the concentrations of oil in sea water which are deleterious to various species. Experimental data, however, are scarce and consequently the toxicology of oil to marine organisms is not well understood.

Nelson (1925) observed marine mollusks (*Mya arenaria*) being destroyed by oil on tidal flats of Staten Island, N.Y. The Pacific coast sea urchin, *Strongylocentrotus purpuratus*, dies in about 1 hour in a 0.1 percent emulsion of diesel oil. After 20 to 40 minutes in this concentration the animals fail to cling to the bottom and may be washed away (North, et al., 1964).

Crude oil absorbed by carbonized sand does not lose its toxicity. This has been shown by laboratory experiments conducted at Woods Hole (Chipman and Galtsoff, 1949). The amount of oil used was limited to the quantity held in the sand, hence no free oil was present in the water. The oil-sand aggregates were placed in containers filled with sea water but never came into contact with the test animals. Four species were bioassayed: the very hardy toadfish (*Opsanus tau*) in the yolk sac stage, the moderately tolerant barnacle (*Balanus balanoides*), and oyster (*Crassostrea virginica*), and the extremely sensitive hydrozoan, (*Tubularia crocea*).

The survival of toadfish embryos was indirectly proportional to the concentration of oil in water.

In a concentration of 0.5 percent, the embryos survived for 13 days (end of test); in 1.25 percent, 8 days; in 2.5 percent, 6 days; and in 5 percent, 4 days. Barnacles suffered 80 to 90-percent mortality within 70 hours in 2.0-percent mixtures of oil in sea water. They became inactive in 23 hours in concentrations of 2 percent and above. *Tubularia* suffered 90 to 100-percent mortality within 24 hours after being placed in water containing a 1:200 oil-carbonized sand aggregate. Water extracts of crude oil were lethal within 24 hours at concentrations of 500 mg/l and greater.

Experiments with oysters consisted primarily of determining the effect of oil adsorbed on carbonized sand on the number of hours the oysters remain open and feeding and on the rate of water transport across the gills. A paste-like aggregate of oil in carbonized sand (50 ml crude oil to 127 g sand) was prepared, wiped clean of excess oil, and placed in the mixing chamber. Sea water was delivered through this chamber to the recording apparatus at a rate slightly in excess of the rate of water transport by oyster gills (Galtsoff, 1964; Chipman and Galtsoff, 1949). There was a noticeable decrease in the number of hours the test oysters remained open and in the daily water transport rate through the gills. The time open was reduced from 95 to 100 percent during the first 4 days of testing to only 19.8 percent on the 14th day. The total amount of water transported per day, and presumably used for feeding and respiration, was reduced from 207 to 310 liters during the first 6 days to only 2.9 to 1 liter per day during the period between the eighth and 14th day of continuous testing. These tests indicate that oil incorporated into the sediments near oyster beds continues to leach water-soluble substances which depress the normal functions of the mollusk.

Critical observations are lacking on the effect of oil on pelagic larvae of marine invertebrates, but there is good reason to assume that crude oil and petroleum products are highly toxic to free-swimming larvae of oysters. Speer (1928) considers that they are killed by contact with surface oil film. Laboratory experience of Galtsoff (unpublished records) shows that oyster larvae from 5 to 6 days old were killed when minor quantities of fuel oil were spilled by ships in the Woods Hole harbor and the contaminated water penetrated into the laboratory sea water supply.

The tests described above leave no doubt that water-soluble substances are leached from oil spilled into water and adversely affect marine life. It is reasonable to assume that the water soluble materials of oil may contain various hydrocarbons, phenols, sulfides, and other substances toxic to

aquatic life. The water-soluble fraction leached from crude oil is easily oxidized by aeration and loses its toxicity (Chipman and Galtsoff, 1949).

Carcinogenic Substances From Oil-Polluted Waters

Presence of hydrocarbons similar to benzopyrene in oil-polluted coastal waters and sediments of France in the Mediterranean was reported by Mallet (1965) and Mallet and Sardou (1965). The effluents from the industrial establishments on the shores at Villefranche Bay comprise tar substances, which contain benzopyrenes, benzo-8, 9-fluoranthene, dibenzanthracenes, chrysene, 10-methyl anthracene, and nitrogenous derivatives such as dimethylbenzocindine. These substances are carried out into the bay water and settle on the bottom. The pollution is augmented by incompletely burned oils discharged by turbine ships. The content of benzopyrene in bottom sediments ranges from 500 micrograms in 100 g sample collected at the depth of 8 to 13 cm to 1.6 micrograms at 200 cm. Similar contamination is of importance in the Gulf of Fos, Etang de Berne, and in the delta of the Rhone River.

Carcinogenic hydrocarbons were found to be stored in plankton of the bay of Villefranche, in concentrations varying from 2.5 to 40 micrograms per 100 g. Fixation of benzopyrenes was found also in the bodies of holothurians (Lalou, 1965) in a bay near Antibes. The reported concentration in the visceral mass of holothurian was slightly higher than that in the bottom sediment.

Observations on storage of carcinogenic compounds found in oil-polluted water are biologically significant. The important question of biological magnification as these compounds are ingested by plankton feeders remains unanswered and needs to be investigated.

Sampling of Oil-Polluted Sea Water

The question of the minimal concentration of oil and petroleum products consistent with uninhibited growth and reproduction of aquatic species is more difficult to answer than it is in the case of other contaminants. As has been shown above, oil is found in water in four distinct phases: (1) surface oil film, (2) emulsion in sea water, (3) extract of water soluble substances, and (4) semi-solid aggregate of oil and sediment covering the bottom. Obviously, no single sample could include all four phases and the method of sampling should

vary accordingly. Collection of samples of a heavy oil slick near the origin of spillage presents no particular difficulty because an adequate quantity may be scooped easily and placed in a proper container. Serious difficulty arises, however, in case of an iridescent film of oil approaching the thickness of a monomolecular layer. Garrett (1964), made a special study of slick-forming materials naturally occurring on sea surfaces and demonstrated their highly complex composition. The collection of very thin layers of surface water was made by means of a specially constructed plastic screen. The entrapped compounds were washed off into a large container (Garrett, 1962). He found surface-acting substances in all areas where the sea surface was altered by monomolecular films and concluded that "a chemical potential exists whereby such surface alterations can occur when conditions are suitable for the adsorption and compression of the surface-active molecules at the air/water boundary." The oil film at the air/water boundary may be composed of several interacting organic compounds. This complexity must be kept in mind in studies of oil pollution in sea water.

If a relatively thick layer of contaminated water is needed, the sample may be scooped or sucked from an area of sea surface enclosed by a floating frame. Interference due to wave ripples is minimized in this way.

For analysis of an oil emulsion in sea water, a sample of a desired volume may be collected by pump or by any type of self-closing water bottle lowered within the surf area.

For obtaining water soluble substances leached from oil sludge, sampling should be made by pumping or by using a water sampler lowered as close as possible to the oil-covered bottom.

Samples of oil adsorbed on sediments can be obtained by using bottom samplers designed to take quantitative samples.

Contamination of beaches by floating tar ballast and cleaning water discharged by ships sailing along our coast is of such common occurrence that at present it is almost impossible to find a public beach free from this nuisance. Cakes of solidified oil tar can be picked by hand from the tidal zone of any beach along the Atlantic and Gulf coasts.

Recommendation: Until more information on the chemistry and toxicology of oil in sea water becomes available, the following requirements are recommended for the protection of marine life. No oil or petroleum products should be discharged into estuarine or coastal waters in quantities that (1) can be detected as a visible film or sheen, or by odor, (2) cause tainting of fish and/or edible invertebrates, (3) form an oil-sludge deposit on the shores or bottom of the receiving

Wildlife

Oil

Waterbirds, muskrats, otters, and many other wildlife species require water that is free of surface oil. Studies by Hartung (1965) demonstrated that egg laying was inhibited when mallards ingested small quantities of oil. When oil from the plumage was coated on mallard eggs, it reduced hatching from 80 to 21 percent. The full significance of this

type of damage to wildlife populations is unknown.

Dramatic losses of waterbirds (ducks, geese, coot, swans, gannets, murres, and others) result from contamination of the plumage by oil from the surface of the water. Once the bird's plumage is soaked with oil, the bird loses its natural insulation to the cold and dies. Many hundreds of thousands of birds have died from oil pollution in some years in North American waters.

Oil that settles to the bottom of aquatic habitats can blanket large areas and destroy the plants and animals of value to waterfowl. Reportedly, some oil sludges on the bottoms of aquatic habitats tend to concentrate pesticides, thus creating a double hazard to waterfowl that would pick up these contaminants in their normal feeding process.

APPENDIX 2
ANIMAL TOXICITY STUDIES

TABLE 1

Animal Toxicity Resulting from
Aerosol Exposure to Oil

Animal	Experimental Data	Results
<u>1. Middle Distillates</u>		
6 albino rats	9600 mg/m ³ aerosol of deodorized kerosene; 6 hr/day for 4 consecutive days	loss of coordination; sluggishness; dermatitis; normal weight gain
25 rats	9600 mg/m ³ aerosol of deodorized kerosene; 6 hr/day, 5 days/wk for 13 weeks	2 died after 16 and 30 days; bronchopneumonia; elevated urine pH; erythrocytopenia; no progressive effects
rats	14,400 mg/m ³ vapors of C ₉ -C ₁₀ aromatic distillate for 7 hours	acute LC ₅₀
rats	3200-5200 mg/m ³ vapors of C ₉ -C ₁₀ aromatic distillate; 18 hr/day; up to 2,424 hours of exposure	decreased rate of weight gain; neutrophilia; lymphocytopenia; decreased total leukocyte count; bilateral cataracts; hemorrhagic lungs, liver, kidneys, spleen; increased myelotic precursors in bone marrow
rats	260-1000 mg/m ³ vapors of C ₉ -C ₁₀ aromatic distillate; 8 hr/day; 5 days/wk; 700 hr. total	no adverse effects
rats	4600 mg/m ³ vapors of C ₁₁ -C ₁₂ aromatic distillate for 7 hours	acute LC ₅₀
37 rats	3200 mg/m ³ vapors of C ₁₁ -C ₁₂ aromatic distillate; 18 hr/day; up to 1,683 hours of exposure	50% died after 18 hr; decreased rate of weight gain; hemorrhagic lungs, liver; splenic dystrophy; decreased total leukocyte count; neutrophilia; lymphocytopenia; watery bone marrow; dermatitis

TABLE 1 (Cont'd)

Animal Toxicity Resulting from
Aerosol Exposure to Oils

Animal	Experimental data	Results
mice	6900 mg/m ³ deodorized kerosene aerosol (duration not specified)	slight depression in breathing rate; no respiratory tract irritation
mice	9700 mg/m ³ vapors of C ₉ -C ₁₀ aromatic distillate; 3.75 hr. exposure	Acute LC ₅₀
mice	3400 mg/m ³ vapors of C ₁₁ -C ₁₂ aromatic distillate; 3.75 hr. exposure	Acute LC ₅₀
3 rhesus monkeys	1000 mg/m ³ vapors of C ₉ -C ₁₀ aromatic distillate; 7 hr/day; 5 days/wk; 90 exposures	hair loss; dry skin; sedation; tremor; leukocytopenia; neutrophilia; lymphocytopenia; decreased erythrocytic and myelocytic precursors in bone marrow
3 rhesus monkeys	260 mg/m ³ of vapors of C ₉ -C ₁₀ aromatic distillate; 7 hr/day; 5 days/wk; 90 exposures	elevated hematocrit; leukocytopenia; neutrophilia; lymphocytopenia
4 rhesus monkeys	300 or 1280 mg/m ³ vapors of C ₁₁ -C ₁₂ of aromatic distillate; 7 hr/day; 5 days/wk; 90 exposures	eye and skin irritation; diarrhea; neutrophilia; lymphocytopenia; increased erythrocytic and decreased myelocytic precursors in bone marrow
beagles	100 mg/m ³ deodorized kerosene aerosol; 6 hr/day; 5 days/wk for 13 weeks	no adverse effects
beagles	20 mg/m ³ given as above	mean weight increase
4 cats	6400 mg/m ³ deodorized kerosene aerosol; 6 hours/day for 14 days	no adverse effects

TABLE 1 (Cont'd)

Animal Toxicity Resulting from
Aerosol Exposure to Oils

Animal	Experimental Data	Results
<u>2. Lubricating Oils</u>		
Acute exposure		
6 albino mice	4330 mg/m ³ aerosol of S.A.E. 10 motor oil; 2 hr exposure	oil retention in terminal bronchioles and alveolar ducts; vigorous oil phagocytosis
7 albino mice	4330 mg/m ³ aerosol of S.A.E. 10 motor oil; 92 hr exposure total (intermittent schedule)	one death; heavy oil retention in all divisions of respiratory tree; pneumonia; coalescence of oil into giant droplets (> 30 diameter)
6 albino mice	4500 mg/m ³ aerosol of S.A.E. 10 motor oil; 2 hr exposure	2 deaths; oil retention in terminal bronchioles and alveolar ducts; vigorous oil phagocytosis
13 albino mice	4500 mg/m ³ aerosol of S.A.E. 10 motor oil; 90 hr exposure total (intermittent schedule)	increased macrophages and foam cells in alveolar lumina and septae; oil deposition in 2 weeks; decreased ATP activity of macrophages; focal oil granulomas and pneumonia in 3 weeks
Chronic exposure		
6 rhesus monkeys	132 mg/m ³ aerosol of S.A.E. 10 motor oil; 100 days; schedule of 30 min aerosol alternating with 30 min air room	3 deaths; oil accumulation in lungs followed by gradual clearing over one year; pneumonia; bronchiolitis; pulmonary fibrosis; pulmonary edema; weight loss; atrophic stomach fur loss
80 white mice	same as for monkeys	gradual accumulation in lung macrophages in peripheral and subpleural alveoli; no free oil; oil macrophages in tracheobronchial lymph nodes; minimal toxicity

TABLE 1 (Cont'd)

Animal Toxicity Resulting from
Aerosol Exposure to Oils

Animal	Experimental Data	Results
120 mice	5 or 100 mg/m ³ aerosol of lubricating oil; 6 hr/day; 5 days/wk; 12 months	lung oil macrophages scattered randomly; no major lung response; no other adverse effects
160 rats	same as for mice	pulmonary tissue damage indicated by elevated lung alkaline phosphatases; progressive interstitial pneumonia only with higher concentration
30 rats	13, 30, or 60 mg/m ³ aerosols of industrial lubricating oils (without additives); 5 hr/day for 6 months	serum neuraminic acid levels increased progressively; decrease of serum albumin and leukocyte phagocytic activity; increased serum globulins
45 rats	same as above	leukopenia; increased parasympathetic tone; decrease in weight gain rate; decreased respiratory rate; increased neuromuscular excitability threshold; pulmonary infiltration and inflammation; liver, kidney, heart and adrenal degeneration

3. White Oils

Acute exposure

20 rats	30,000 mg/m ³ aerosol of mineral oil 6 hr/day for 3 weeks	increased macrophages and foam cells in alveolar lumina and septae; oil deposition in 2 weeks; decreased ATP activity of macrophages; focal oil granulomas and pneumonia in 3 weeks
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TABLE 1 (Cont'd)

Animal Toxicity Resulting from
Aerosol Exposure to Oils

Animal	Experimental Data	Results
Chronic Exposure		
218 hamsters	5 or 100 mg/m ³ aerosol of mineral oil; 5 days/wk; 6 hr/day; 26 months	no major lung tissue response; presence of oil macrophages in alveoli; no other pathological findings
46 rabbits	same as above	no adverse effects
18 dogs	same as above	pulmonary tissue damage indicated by elevated lung alkaline phosphatases; scattering and coalescence of oil droplets in lungs; granulomas with intra- cellular oil droplets

TABLE 2

Animal Toxicity Resulting from
Dermal Exposure to Oil

Animal	Experimental Data	Results
<u>1. Middle Distillates</u>		
Wistar rats	undiluted diesel fuel applied to tail skin 6 hr/day for 10 days	dermatitis; hair loss; decreased hemoglobin; erythrocytopenia; reticulocytosis; leukocytosis; neutrophilia; lymphocytopenia
5 albino guinea pigs	diesel fuel applied to intracapsular skin 5 times/wk for 19 days	erythema; desquamation; hair loss; ulceration; and crusting
albino guinea pigs	various petroleum fuel distillates applied to skin every other day; 4 applications total	hyperplasia; hyperkeratosis; hair loss; aromatic fuels more toxic than paraffinic fuels
20 guinea pigs	Landsteiner and Jacobs skin sensitization method with diesel fuel	no skin sensitization
10 white Belgian rabbits	Draize method with diesel fuel	mild primary irritant to skin and conjunctiva
79 mice	0.10-0.15 g/animal of C ₉ -C ₁₂ aromatic distillate applied to skin 3 times/wk; 150 applications total	dry, thick, scaly skin; hyperkeratosis; epidermal atrophy; dermatitis; ulceration
100 mice	intrascapular skin; daily application of light grade diesel fuels	dermatitis

Animal Toxicity Resulting from
Dermal Exposure to Oil

Animal	Experimental Data	Result
<u>2. Lubricating Oils</u>		
albino guinea pigs	0.6 ml/animal of yellow lubricating oil	desquamation and hyperkeratosis
<u>3. White Oils</u>		
two Holstein Friesian calves	0.13 ml/kg of body-weight/day of white lubricating oil for 8 weeks applied to skin	no gross skin pathology
albino guinea pigs	0.6 ml/animal of white lubricating oil applied to skin every other day for 4 days	slight erythema and desquamation

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TABLE 3

Animal Toxicity Resulting from
Oral Administration of Oils

Animal	Experimental Data	Results
<u>1. Middle Distillates</u>		
Wistar rats	20-25 ml/kg of body-weight/day diesel oil by gastric intubation for 14 days	hemoglobinemia; reticulocytosis; neutrophilia; lymphocytopenia; thrombocytopenia; elevated serum malate dehydrogenase, aspartate and alanine aminotransferase
138 Wistar rats	16.0 ml/kg of body-weight diesel oil by gastric intubation	acute oral LD ₅₀
5 Wistar rats	6.9 ml/kg of body-weight/day diesel oil by gastric intubation for approx. 3 weeks	subacute LD ₅₀
10 rabbits	1.0 ml/kg of body-weight of fuel oil orally	23% drop in blood sugar in 5-7 hr; return to normal levels by 12 hr.
cow	approx. 7 liters of diesel fuel ingested accidentally	low grade fever; diarrhea; constipation; lowered milk production; stiff uncertain gait; swelling of hind fetlocks; recovery in 8 days
ewe	ingestion of diesel fuel-soaked grass	weakness; weight loss; nodular lesions on inner rumen wall; complete loss of fleece; neutrophilia;
<u>2. Lubricating Oils</u>		
mice	chronic ingestion of spindle oil for 20-90 weeks (dose not specified)	fatty infiltration and degeneration of liver, spleen, ovary and adrenals

TABLE 3 (Cont'd)

Animal Toxicity Resulting from
Oral Administration of Oils

Animal	Experimental Data	Results
<u>3. White oils</u>		
mice	20 ml/kg of body-weight/day of white mineral oil ingested with diet	rough, dry skin; pilo-erection; restlessness; weight loss in 5 days; all died by 7 days; fatty degeneration of liver; proliferation of reticulo-endothelial cells of spleen; epidermal hyperkeratosis; renal tubular degeneration
rats	5 ml/kg of body-weight/day of white mineral oil ingested with diet	same as above in mice
1 monkey	2.2 ml/kg of body-weight/day of white mineral oil in diet; total consumption 96 ml	weight loss; diarrhea; death in 3 weeks; hepatic and renal congestion; ulceration and inflammation of colon, heart, lung and spleen
1 monkey	1.1 ml/kg of body-weight/day of white mineral oil in diet; total consumption 36 ml	diarrhea; weight loss; death in 11 days; same pathological findings as above
1 monkey	1.1 ml/kg of body-weight/day of white mineral oil in diet; total consumption 195 ml in 3 months	no adverse effects; slight hepatic and renal congestion

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