

ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

OIL, USED MOTOR OIL ENTRY

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Like a library or many large databases (such as EPA's national STORET water quality database), this document contains information of variable quality from very diverse sources. In compiling this document, mistakes were found in peer reviewed journal articles, as well as in databases with relatively elaborate quality control mechanisms [366,649,940]. A few of these were caught and marked with a "[sic]" notation, but undoubtedly others slipped through. The [sic] notation was inserted by the editors to indicate information or spelling that seemed wrong or misleading, but which was nevertheless cited verbatim rather than arbitrarily changing what the author said.

Most likely additional transcription errors and typos have been added in some of our efforts. Furthermore, with such complex subject matter, it is not always easy to determine what is correct and what is incorrect, especially with the "experts" often disagreeing. It is not uncommon in scientific research for two different researchers to come up with different results which lead them to different conclusions. In compiling the Encyclopedia, the editors did not try to resolve such conflicts, but rather simply reported it all.

It should be kept in mind that data comparability is a major problem in environmental toxicology since laboratory and field methods are constantly changing and since there are so many different "standard methods" published by EPA, other federal agencies, state agencies, and various private groups. What some laboratory and field investigators actually do for standard operating practice is often a unique combination of various standard protocols and impromptu "improvements." In fact, the interagency task force on water methods concluded that [1014]:

It is the exception rather than the rule that water-quality monitoring data from different programs or time periods can be compared on a scientifically sound basis, and that...

No nationally accepted standard definitions exist for water quality parameters. The different organizations may collect data using identical or standard methods, but identify them by different names, or use the same names for data collected by different methods [1014].

Differences in field and laboratory methods are also major issues related to (the lack of) data comparability from media other than water: soil, sediments, tissues, and air.

In spite of numerous problems and complexities, knowledge is often power in decisions related to chemical contamination. It is therefore often helpful to be aware of a broad universe of conflicting results or conflicting expert opinions rather than having a portion of this information arbitrarily censored by someone else. Frequently one wants to know of the existence of information, even if one later decides not to use it for a particular application. Many would like to see a high percentage of the information available and decide for themselves what to throw out, partly because they don't want to seem uninformed or be caught by surprise by potentially important information. They are in a better position if they can say: "I knew about that data, assessed it based on the following quality assurance criteria, and decided not to use it for this application." This is especially true for users near the end of long decision processes, such as hazardous site cleanups, lengthy ecological risk assessments, or complex natural resource damage assessments.

For some categories, the editors found no information and inserted the phrase "no information found." This does not necessarily mean that no information exists; it

simply means that during our efforts, the editors found none. For many topics, there is probably information "out there" that is not in the Encyclopedia. The more time that passes without encyclopedia updates (none are planned at the moment), the more true this statement will become. Still, the Encyclopedia is unique in that it contains broad ecotoxicology information from more sources than many other reference documents. No updates of this document are currently planned. However, it is hoped that most of the information in the encyclopedia will be useful for some time to come even without updates, just as one can still find information in the 1972 EPA Blue Book [12] that does not seem well summarized anywhere else.

Although the editors of this document have done their best in the limited time available to insure accuracy of quotes or summaries as being "what the original author said," the proposed interagency funding of a bigger project with more elaborate peer review and quality control steps never materialized.

The bottom line: The editors hope users find this document useful, but don't expect or depend on perfection herein. Neither the U.S. Government nor the National Park Service make any claims that this document is free of mistakes.

The following is one chemical topic entry (one file among 118). Before utilizing this entry, the reader is strongly encouraged to read the README file (in this subdirectory) for an introduction, an explanation of how to use this document in general, an explanation of how to search for power key section headings, an explanation of the organization of each entry, an information quality discussion, a discussion of copyright issues, and a listing of other entries (other topics) covered.

See the separate file entitled REFERENC for the identity of numbered references in brackets.

HOW TO CITE THIS DOCUMENT: As mentioned above, for critical applications it is better to obtain and cite the original publication after first verifying various data quality assurance concerns. For more routine applications, this document may be cited as:

Irwin, R.J., M. VanMouwerik, L. Stevens, M.D. Seese, and W. Basham. 1997. Environmental Contaminants Encyclopedia. National Park Service, Water Resources Division, Fort Collins, Colorado. Distributed within the Federal Government as an Electronic Document (Projected public availability

on the internet or NTIS: 1998).

Oil, Used Motor Oil (Used Crankcase Oil)

Brief Introduction:

Br.Class: General Introduction and Classification Information:

Waste crankcase oil (WCO) is defined as used lubricating oils removed from the crankcase of internal combustion engines. Before they are used, crankcase oils consist of a base lubricating oil (a complex mixture of hydrocarbons, 80 to 90% by volume) and performance-enhancing additives (10 to 20% by volume). Crankcase oils are altered during use because of the breakdown of additives, contamination with the products of combustion, and the addition of metals from the wear and tear of the engine. Therefore, the composition of waste oil is difficult to generalize in exact chemical terms. It is recognized that the major components consist of aliphatic and aromatic hydrocarbons (such as phenol, naphthalene, benz(a)anthracene, benzo(a)pyrene, and fluoranthene) [752].

According to the US Coast Guard Emergency Response Notification System (ERNS), used motor oil is one of the most commonly spilled petroleum products in the U.S. [635]. See Fate/Detail section below for more information on spills and other routes of entry into the environment.

Lubricating oils are relatively heavy products. Petroleum distillates in order of decreasing volatility include [363]:

1. Petroleum ether or benzine
2. Gasoline
3. Naphtha
4. Mineral spirits
5. Kerosene
6. Fuel oils
7. Lubricating oils
8. Paraffin wax
9. Asphalt or tar.

The CAS number given for used motor oil by ATSDR, 8002-05-09 [961], is incorrect; that CAS number is used for petroleum in general or crude oil [617].

Br.Haz: General Hazard/Toxicity Summary:

New motor oil contains fresh and lighter hydrocarbons that would be more of a concern for short-term (acute) toxicity to aquatic organisms, whereas used motor oil

contains more metals and heavy polycyclic aromatic hydrocarbons (PAHs) that would contribute to chronic (long-term) hazards including carcinogenicity (see Chem.Detail section below). Metals of concern include lead; and often to a lesser degree, zinc, chromium, barium, and arsenic [752].

Aromatics are considered to be the most acutely toxic component of petroleum products, and are also associated with chronic and carcinogenic effects [770]. Aromatics are often distinguished by the number of rings they possess, which may range from one to five [770]. Lighter, mono-aromatics (one ring) compounds include benzene, toluene, ethylbenzene, and xylenes [771]. Aromatics with two or more rings are referred to as polyaromatic hydrocarbons (PAHs) [770]. Waste crankcase oil contains several toxic components including up to 30% aromatic hydrocarbons, with as much as 22 ppm benzo(a)pyrene (a PAH) [75].

In a recent Upshall et al (1993) study, used motor oil had a density of 0.828 g/ml and contained 14% aromatics and 65.4% aliphatics (by weight) [519]. In this study, the sum of 26 individual PAHs represented 0.17% of the oil, or 1.2% of the aromatic fraction [519].

Above paragraph text reprinted with permission from Environmental Toxicology and Chemistry, Volume 12(11), C. Upshall, J.F. Payne, and J. Hellou, "Induction of MFO Enzymes and Production of Bile Metabolites in Rainbow Trout (*Oncorhynchus mykiss*) Exposed to Waste Crankcase Oil." Copyright 1993 SETAC].

Used motor oil typically has much higher concentrations of PAHs than new motor oil [40,519].

Chronic effects of naphthalene, a constituent in used motor oil, include changes in the liver and harmful effects on the kidneys, heart, lungs, and nervous system [766]. Due to their relative persistence and potential for various chronic effects (like carcinogenicity), PAHs (and particularly the alkyl PAHs) can contribute to long term (chronic) hazards of jet fuels in contaminated soils, sediments, and groundwaters (see "PAHs as a group entry," individual PAH entries, and metals entries).

Additional human health issues related to used mineral-based crankcase oil have been summarized by ATSDR [961]. Due to lack of time, the ATSDR document has not yet been adequately summarized herein.

Br.Car: Brief Summary of Carcinogenicity/Cancer Information:

While an oil is being used in a crankcase, it breaks down to give a wide variety of oxygenated and aromatic hydrocarbons [497]. Like several individual PAHs, waste crankcase oil has been shown to be mutagenic and teratogenic [75].

Combustion-derived PAHs have been linked to mutagenesis and carcinogenesis, and some heavy metals have a toxic effect. The 4- to 7-ring PAHs have been especially implicated in the carcinogenic effect of used oil [519].

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The debates on which PAHs, alkyl PAHs, and other aromatics and metals in complex mixtures such as this product to classify as carcinogens, and the details of exactly how to perform both ecological and human risk assessments on the complex mixtures typically found at contaminated sites, are likely to continue. There are some clearly wrong ways to go about it, but defining clearly right ways is more difficult. PAHs in used motor oil occur in complex mixtures rather than alone. Perhaps the most unambiguous thing that can be said about complex mixtures of PAHs and other aromatics found in used oil is that such mixtures are often carcinogenic and possibly phototoxic. One way to approach site specific risk assessments would be to collect the complex mixture of PAHs and other lipophilic contaminants in a semipermeable membrane device (SPMD, also known as a fat bag) [894,895,896], retrieve the contaminant mixture from the SPMD, then test the mixture for carcinogenicity, toxicity, and phototoxicity (James Huckins, National Biological Service, and Roy Irwin, National Park Service, personal communication, 1996).

See also: PAHs as a group entry.

Additional human health issues related to used mineral-based crankcase oil have been summarized by ATSDR [961].

Br.Dev: Brief Summary of Developmental, Reproductive, Endocrine, and Genotoxicity Information:

Like several individual PAHs, waste crankcase oil has been shown to be mutagenic and teratogenic [75]. The results are mixed, but some immunological, reproductive, fetotoxic, and genotoxic effects have been associated

with a few of the compounds found in used motor oil (see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture).

Exposure to used crankcase oil has been shown to produce an induction of EROD enzymes in the liver of fish [519]. Crankcase oil also demonstrated some effects on amphibian reproduction [763].

A study was conducted to determine the effects of waste crankcase oil on amphibian reproduction, using the green treefrog (*Hyla cinerea*). Egg hatching success, tadpole growth, and successful metamorphosis were measured in four concentrations of oil. The effects of oil as a food source was also studied. Hatching success was not measurably influenced by the presence of oil. Tadpole and alga growth were negatively associated with the presence of oil. No tadpoles from the high concentration of oil treatments successfully metamorphosed [763].

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See also: PAHs as a group entry.

Br.Fate: Brief Summary of Key Bioconcentration, Fate, Transport, Persistence, Pathway, and Chemical/Physical Information:

Hydrocarbons from oil can move to atmosphere or settle through water to bottom sediments, where they may persist for years [961]. Metals from oil may build up in various media [961].

The concentration of various PAHs is much higher in used oil than in (fresh) lubricating oil [519]. For example, Grimmer et al. reported concentrations of dibenz(a,c)-anthracene, 4-methylpyrene, fluoranthene, benz(a)anthracene, benzo(e)pyrene, benzo(g,h,i)perylene, and benzo(a)pyrene, respectively, 36, 49, 253, 720, 1,112, 4,770, and 7,226 times higher in "used" compared to "fresh" oil [519].

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Exposed to Waste Crankcase Oil." Copyright 1993 SETAC].

As an oil used in a crankcase, motor oil breaks down to give a wide variety of oxygenated and aromatic hydrocarbons [497]. Other organic compounds found in waste oil include toluene, benzene, xylenes, and ethylbenzene. Also present are organic and inorganic compounds of chlorine, sulphur, phosphorus, bromine, nitrogen, and metals such as zinc, magnesium, barium, and lead resulting from oil additives and contamination during use or disposal [752].

Used engine oil is a contaminant of concern, with large volumes entering aquatic ecosystems through water runoff. The major source of petroleum contamination in urbanized estuaries comes from waste crankcase oil [762]. PAHs, heavy metals, additives and antioxidants, trace levels of chlorinated solvents, and PCBs have been detected in used engine oil [519]. As mentioned above, naphthalene, benzo(a)pyrene, fluorene, and phenanthrene are common PAH components of used motor oil [75].

Used crankcase oil was identified as the main source of PAHs and related sulfur heterocyclics in stormwater in Philadelphia, PA [207]. In rural areas a considerable portion of PAHs in streams comes from highways [43]. The amount of WCOs lost by runoff is variable and estimates range from 3 to 5% to > or = 20%. In general, high runoff rates are expected when roads are made of non-porous materials such as clay, when roads are in poor condition, and following periods of heavy rainfall. The compounds detected in runoff of WCOs included metals such as zinc, aluminum, sodium, and calcium, and organic compounds such as phenol and chlorophenol. Compounds in runoff of WCOs may be in the water-soluble fraction, or may be adsorbed to particles in the runoff [752]. Crankcase oil drippings in parking lots are a major source of hydrocarbons in urban areas. Of the total hydrocarbons generated from parking lots surfaces in storm runoff, 64% are in the form of settleable solids. The use of detention basins to capture runoff and allow settling is an effective and economical way to reduce pollutant impact on receiving waters. One study determined that treatment of hydrocarbons, PAHs, and suspended solids by a detention pond was 70, 14, and 36 percent better, respectively, than treatment efficiencies of a combined sanitary/storm municipal treatment plant studied in Providence, Rhode Island [763].

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metamorphosis." Copyright 1994 SETAC].

Another source of WCOs entering the aquatic environment is through improper disposal of used motor oil. Many people change their own car motor oil instead of having it done professionally. Shops that perform oil changes have special receptacles for used motor oil. Many private citizens do not dispose of their used oil properly. For example, some people pour waste oil over their gravel/dirt driveways to keep the dust down, let it sit in their garage or backyard for extended periods of time, or illegally pour it down storm drains. In a 1980 survey of residents living in Providence, Rhode Island, it was estimated that 44 metric tons of waste automobile-lubricating (crankcase) oil generated by the residents was dumped onto roads and into storm sewers [763].

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Citizens or businesses who illegally pour used motor oil into storm drains are polluting urban rivers with PAHs. Citizens should be advised that waste oil should be disposed of properly (contact an auto parts store, local government, and/or auto service shop to find the location of the nearest drop-off).

Additional fate issues related to used mineral-based crankcase oil have been summarized by ATSDR [961].

See also: PAHs as a group entry.

Synonyms/Substance Identification:

Used Motor Oil
Used Crankcase Oil
Waste Crankcase Oils (WCOs) [752]
Waste Oil
Lubricating Oil (Used Crankcase Oil) [560]
Used motor oil 10W30 [560]
Auto Lube (used) [856]
Mineral-based used crankcase oil [961].

Associated Chemicals or Topics (Includes Transformation Products):

See also individual entries:

Oil, New or Unused Motor Oil
Oil Spills
Petroleum, General

PAHs as a group
Naphthalene
Benzo(a)pyrene
Fluorene
Fluoranthene
Phenanthrene

Water Data Interpretation, Concentrations and Toxicity (All Water Data Subsections Start with "W."):

W.Low (Water Concentrations Considered Low):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

W.High (Water Concentrations Considered High):

The concentrations of waste crankcase oils and its components found in the environment is governed to a large extent by the entry scenario that lead to its release [752]:

As a result of used motor oil being used in the re-refining process: A monitoring study of wastewater effluents from a waste oil re-refinery in the United States (location not specified) found that the mean concentration of metals varied from 0.34 mg/L for cadmium to 271 mg/L for lead. Other metals detected in wastewater were arsenic (3.4 mg/L), chromium (10 mg/L), barium (80 mg/L), and zinc (250 mg/L). For organic compounds, mean concentrations varied from below the detection limit (DL = 0.02 mg/L) for benzo(a)anthracene and benzo(a)pyrene to 1306 mg/L for toluene. Other organics detected in wastewater were naphthalene (283 mg/L), benzene (364 mg/L), and several chlorinated solvents (309 to 666 mg/L) [752].

As a result of used motor oil being used for dust suppression: An Ontario field study of a road treated with waste oil demonstrated that the water soluble fraction (WSF) (in this study, the WSF was measured for water-soluble hydrocarbon content) concentration in a nearby stream increased from 23 mg WSF/L of water before application, to 60 mg WSF/L of water one week after application. Three months after the waste oil application, a concentration of 350 mg WSF/L was found in runoff water from the road. In a follow up study, they observed that the WSF concentration in a nearby stream increased from 24 mg WSF/L before

application to 50 mg WSF/L in upstream samples, and from 17 mg WSF/L before application to 63 mg WSF/L in downstream samples one month after application. The lead concentration in runoff water from the road was 0.06 mg/L about two months after application of waste crankcase oil. Similarly, a lead concentration of 0.1 mg/L was detected in a stream located approximately 500 meters from the road, four months after application [752].

W. Typical (Water Concentrations Considered Typical):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

W. Concern Levels, Water Quality Criteria, LC50 Values, Water Quality Standards, Screening Levels, Dose/Response Data, and Other Water Benchmarks:

W. General (General Water Quality Standards, Criteria, and Benchmarks Related to Protection of Aquatic Biota in General; Includes Water Concentrations Versus Mixed or General Aquatic Biota):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

W. Plants (Water Concentrations vs. Plants):

The most sensitive effects observed for freshwater species involved algal communities exposed to WCOs under natural light during summer and autumn in a greenhouse in New Jersey, United States. Under flow-through conditions, a five-week summer exposure to the water soluble fraction (WSF) of WCOs (0.038 mg WSF/L) resulted in decreases in chlorophyll a and chlorophyll c concentrations (in this study, chlorophyll c is used as an indicator of diatom biomass) and a slight increase in phycocyanin concentration (indicative of blue-green algal abundance). As a result, a shift in community structure (reduction in diversity and abundance) was observed after the exposure period. When exposed to the WSF (0.065 mg WSF/L water) of WCOs for five weeks under autumn conditions, similar effects were observed. In this study, the WSF was measured for water-soluble hydrocarbon content [752].

W. Invertebrates (Water Concentrations vs. Invertebrates):

Invertebrates are the most sensitive marine species to the water-soluble fraction of WCOs. The clam *Mercenaria* sp. had a 48h LC50 of 0.04 mg WSF/L (measured for water-soluble hydrocarbon content) for the embryo and a 48h LC50 of 0.1 mg WSF/L water (measured for water-soluble hydrocarbon content) for the larvae under static conditions [752].

Acute toxicity of motor oils to *Artemia*. These fluorescence tests were older Canadian methods using only the product indicated and would be only roughly comparable to other fluorescence values. Fluorescence methods are not particularly desirable when unknown or mixed oil products are of concern (ranges in parentheses) [684]. The following tables show that new motor oil has more potential for acute (short term) toxicity than used motor oil; however, these findings do not relate to overall hazard since used motor oil contains more metals and heavy PAHs that would contribute to chronic (long-term) hazards including carcinogenicity. See also the "Petroleum, General" entry for comparison with 21 other refined and crude oils.

OIL	48-Hr EC50 (Measured by fluorescence in MG/L)
Auto Lube (New)	0.08 (0-1.51)
Auto Lube (Used)	>12.8

OIL	48-Hr LC50 (Measured by fluorescence in MG/L)
Auto Lube (New)	0.44 (0.1-0.79)
Auto Lube (Used)	>12.8

Acute toxicity of motor oils to *Daphnia magna*. Data from all valid replicates were combined (ranges in parentheses) [684]. Same remarks apply as for the table above. See also the "Petroleum, General" entry for comparison with 21 other refined and crude oils.

48-Hr EC50
(Measured by
fluorescence

MOTOR OIL	in MG/L)
Auto Lube (New)	0.3 (0.25-0.34)
Auto Lube (Used)	4.65 (3.36-5.97)
	48-Hr LC50 (Measured by fluorescence in MG/L)
MOTOR OIL	
Auto Lube (New)	0.38 (0.32-0.44)
Auto Lube (Used)	4.87 (3.36-5.97)

W.Fish (Water Concentrations vs. Fish):

Routes of Exposure [519, Reprinted with permission from Environmental Toxicology and Chemistry, Volume 12(11), C. Upshall, J.F. Payne, and J. Hellou, "Induction of MFO Enzymes and Production of Bile Metabolites in Rainbow Trout (*Oncorhynchus mykiss*) Exposed to Waste Crankcase Oil." Copyright 1993 SETAC]:

Fish can be exposed to contaminants through their diet or skin, but the major route of exposure to water-soluble compounds is believed to be through the gills. Ingestion of contaminants adsorbed to particulates can be substantial (especially in marine species drinking water), but it is of interest to estimate exposure via the gills. According to Kiceniuk and Jones, the ventilation rate of trout measuring between 10 and 70 grams can be estimated at 2 to 15 ml/min. The oil used in our investigation had a density of 0.828 g/ml and contained 14% aromatics and 65.4% aliphatics (by weight). Therefore we can transform the volume of used crankcase oil that was orally injected into the fish to a time of exposure at concentrations reported in environmental cases.

Blanket statements have been made that toxicity to aquatic life is seldom found in response to oil concentrations below 10 ppb [563]; however, this may be an oversimplification when the full spectrum of potential effects (rather than just acute toxicity) is taken into account.

For freshwater species, the 96-hr LC50 for American flagfish and fathead minnow ranged from 1 to 9.5 mg WSF/L water (flow-through,

measured for water-soluble hydrocarbon and metal contents) [752].

Acute Toxicity, Oil in Water Emulsion (mg/L) [560]:

Genus/Species	96h LC50
Juvenile American Flyfish	4.85 #1
(sic) Flatfish?	0.827 #2

#1. Static test

#2. Flow through test

W.Wildlife (Water Concentrations vs. Wildlife or Domestic Animals):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

W.Human (Drinking Water and Other Human Concern Levels):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

W.Misc. (Other Non-concentration Water Information):

Misc. references (Steve Cinnamon, National Park Service, Personal Communication, 1996):

Chmura, Gail L. and Ross, Neil W. "The Environmental Impacts of Marinas and Their Boats: A literature Review with Management Considerations." Rhode Island Department of Environmental Management and Marine Advisory Service. pp. 1-36

Jackivicz, Thomas P. and Kuzminski, Lawrence N. 1973. "The Effects of the Interaction of Outboard Motors with the Aquatic Environment - A Review." Environmental Research. pp 436-454.

Mastran, Trina A., Dietrich, Andrea M., Gallagher, Daniel L., and Grizzard, Thomas J. November 1994. "Distribution of Polyaromatic Hydrocarbons in the Water Column and Sediments of a Drinking Water Reservoir with Respect to Boating Activity." Water Research. Vol. 39, No. 2, pp. 123-5.

National Geographic. May 1995. "Powerboats will Soon Leave a Cleaner Wake." P.51.

Wachs, Bodo, Wagner, Helmut and Van Donkelaar, Pieter. March 1991. "Two-stroke Engine Lubricant Emissions in a Body of Water Subjected to Intensive Outboard Motor Operation." The Science of the Total Environment. Vol. 116, pp. 59-81.

Wright, David O. and Wagner, Kenneth J. December 1991. "Power boats on shallow lakes: A brief summary of literature and experience on Lake Mohegan." Lake Line. Vol. 11, No. 4, pp. 8-12.

No other information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Sediment Data Interpretation, Concentrations and Toxicity (All Sediment Data Subsections Start with "Sed."):

Sed.Low (Sediment Concentrations Considered Low):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Sed.High (Sediment Concentrations Considered High):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Sed.Typical (Sediment Concentrations Considered Typical):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Sed.Concern Levels, Sediment Quality Criteria, LC50 Values, Sediment Quality Standards, Screening Levels, Dose/Response Data and Other Sediment Benchmarks:

Sed.General (General Sediment Quality Standards, Criteria, and Benchmarks Related to Protection of Aquatic Biota in General; Includes Sediment Concentrations Versus Mixed or General Aquatic Biota):

No information found; see Chem.Detail section for

compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Sed.Plants (Sediment Concentrations vs. Plants):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Sed. Invertebrates (Sediment Concentrations vs. Invertebrates):

Abstract [762]:

The present study provides evidence that relatively low doses of waste crankcase oil (WCO), the predominant petroleum product in runoff and combined sewer overflow discharges, induces measurable sublethal morphological changes in the amphipod *Melita nitida* Smith, an epibenthic estuarine species. Adults were exposed to 1, 10, and 100 ppm WCO mixed in sediments. Adult male and female survivorship was not reduced by exposure to these doses. Juveniles maintained at 1 and 10 ppm survived but juveniles maintained at 100 ppm died within 2 days of emergence from the female. Reproductive females developed abnormal oostegite seta in WCO. The proportion of females developing abnormalities was directly correlated with the concentration of the WCO.

Sed.Fish (Sediment Concentrations vs. Fish):

Collier and Varanasi exposed English sole to sediment extracts containing 0.0104 mg of PAHs (sum of 22 PAHs) per gram sediment and to B(a)P (fish weighing 69 g at 13 degrees C). A fourfold induction of AHH enzymes was observed in liver, with a B(a)P dose of 0.1 mg/kg and with 0.01 mg/kg of PAHs in sediments. In our study, a threefold induction of EROD enzymes was observed in liver, when fish were exposed to a concentration of total unsaturated compounds between 0.2 to 1.7 g/kg (150 ul of used oil). When polycyclic aromatic compounds (PACs) are expressed as a sum of 26 components, this concentration translates into 3.0 to 21 mg/kg, or into 25 to 176 ug/kg if expressed in terms of B(a)P. Comparison of these two mixtures of chemicals, crankcase and contaminants

in sediments, points to 300 to 2,100 times stronger effects from the contaminants in sediments than from crankcase (0.01 compared to 3.0-21 mg/kg). However, if the level of B(a)P is included in the comparison, there is hardly any difference in concentrations (0.1 compared to 0.025-0.176 mg/kg). Again, this comparison neglects the effect of other variables [519].

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Sed.Wildlife (Sediment Concentrations vs. Wildlife or Domestic Animals):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Sed.Human (Sediment Concentrations vs. Human):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Sed.Misc. (Other Non-concentration Sediment Information):

Some of the literature on sediment contamination by petroleum hydrocarbons was summarized in Olsen's 1984 annotated bibliography of the effects of contaminated sediments on fish and wildlife [449].

Between 1990 and 1991, sediment samples taken from water immediately downstream from a motorway in England revealed significantly elevated levels of inorganics (lead, zinc, chromium, copper, nickel, aluminum, calcium, and magnesium), total aromatic hydrocarbons, and PAHs, all of which have been detected in waste crankcase oils. The number of macroinvertebrate taxa was significantly reduced downstream. The change in community structure resulted in a shift from a mixed trophic community (gammarid shrimps and snails) at the upstream control station to a community dominated by collectors (chironomid larvae and tubificid worms). Also, the

consumption of leaf material by the shredder *Gammarus pulex* placed in-situ at the downstream station was significantly reduced compared to the upstream station. Toxicity tests performed with sediment samples collected from the upstream and downstream stations demonstrated that downstream sediment was significantly more toxic to the amphipod *Gammarus pulex* than the upstream sediment. The observed toxicity was attributed to the presence of aromatic hydrocarbons in the sediment [752].

Soil Data Interpretation, Concentrations and Toxicity (All Soil Data Subsections Start with "Soil."):

Soil.Low (Soil Concentrations Considered Low):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Soil.High (Soil Concentrations Considered High):

In a follow up field study of a road treated with waste oil, researchers observed that four months after application, the hexane-extractable material (constituents of WCOs soluble in hexane) concentration in soil where runoff entered the field was higher (0.34 mg/g dry weight) than the concentration observed in a control site (0.15 mg/g dry weight) [752].

Soil.Typical (Soil Concentrations Considered Typical):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Soil.Concern Levels, Soil Quality Criteria, LC50 Values, Soil Quality Standards, Screening Levels, Dose/Response Data and Other Soil Benchmarks:

Soil.General (General Soil Quality Standards, Criteria, and Benchmarks Related to Protection of Soil-dwelling Biota in General; Includes Soil Concentrations Versus Mixed or General Soil-dwelling Biota):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Soil.Plants (Soil Concentrations vs. Plants):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Soil.Invertebrates (Soil Concentrations vs. Invertebrates):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Soil.Wildlife (Soil Concentrations vs. Wildlife or Domestic Animals):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Soil.Human (Soil Concentrations vs. Human):

No information found on this complex and variable mixture. See Chem.Detail section for chemicals found in this product, then look up information on each hazardous compound. Some individual compounds found in petroleum products have low-concentration human health benchmarks for soil (see individual entries on aromatics and entries on metals).

Soil.Misc. (Other Non-concentration Soil Information):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound and III entries for summaries of information on individual components of this mixture.

Tissue and Food Concentrations (All Tissue Data Interpretation Subsections Start with "Tis."):

Tis.Plants:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Plants:

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound and III entries for summaries of information on individual components of this

mixture.

B) Body Burden Residues in Plants: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound and III entries for summaries of information on individual components of this mixture.

Tis.Invertebrates:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Invertebrates:

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound and III entries for summaries of information on individual components of this mixture.

B) Concentrations or Doses of Concern in Food Items Eaten by Invertebrates:

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound and III entries for summaries of information on individual components of this mixture.

C) Body Burden Residues in Invertebrates: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound and III entries for summaries of information on individual components of this mixture.

Tis.Fish:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Fish (Includes FDA Action Levels for Fish and Similar Benchmark Levels From Other Countries):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound and III entries for summaries of information on individual components of this mixture.

B) Concentrations or Doses of Concern in Food Items Eaten by Fish:

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound and III entries for summaries of information on individual components of this mixture.

C) Body Burden Residues in Fish: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

Rainbow Trout Exposed to Crankcase Oil [519, Reprinted with permission from Environmental Toxicology and Chemistry, Volume 12(11), C. Upshall, J.F. Payne, and J. Hellou, "Induction of MFO Enzymes and Production of Bile Metabolites in Rainbow Trout (*Oncorhynchus mykiss*) Exposed to Waste Crankcase Oil." Copyright 1993 SETAC]:

It is difficult to assess the toxicological significance of complex mixtures of contaminants in the environment because of paucity of dose-response studies. Rainbow trout (*Oncorhynchus mykiss*) were exposed per os to waste crankcase oil and analyzed for hydrocarbon classes, 26 polycyclic aromatic compounds (PACs) and 66 elements. MFO enzyme activity, measured as 7-ethoxyresorufin O-deethylase (EROD) was induced in liver, kidney, and heart.

Note from Roy Irwin: per os (in the mouth) in this case meant a syringe attached to a piece of tubing was placed in the mouth of the fish, and the dose was injected directly into the fish's stomach; this exposure was meant to roughly simulate a short term/high water concentration dose exposure such as might occur after a spill, not a longer term exposure in the environment (author J. Hellou, personal communication to Roy Irwin).

The threshold level for induction in liver was approximately 3 mg of PACs (sum of 26 PACs) per kilogram fish. A dose-response study, liver, kidney, and heart MFO activity increased (14-, 5-, and 3-fold, respectively), reaching a maximum between days 1 and 4, then decreased to basal levels by day 12. Analysis of bile metabolites, as glucuronide and sulfate conjugates, showed a pattern similar

to that displayed by MFO induction, possibly with a slight delay. This study establishes time- and dose-response relationships for MFO enzyme induction and appearance of bile metabolites in fish exposed to an environmentally important source of PAC's [519].

Rainbow trout (*O. Mykiss*) were exposed to increasing concentrations of oil to determine the EROD induction potential of this mixture. Enzyme activity was measured in hepatic and extrahepatic tissues 3 days following exposure. A linear increase in EROD activity was observed in both liver ($r=0.9047$, 5% level of significance) and kidney ($r=0.9077$, 5% level of significance) with exposure to increasing concentrations of waste crankcase oil. Induction was much higher in liver than kidney, whereas no induction was observed in the heart ($r=-0.3468$, nonsignificant). Induction occurred with 20 ul of waste crankcase oil (33-230 mg unsaturated fraction of crankcase oil per kilogram of fish) in liver and kidney. Pesonen et al. have also shown increased EROD activity in immature rainbow trout liver and kidney with increasing amounts of beta-naphthoflavone, an MFO-inducing compound (0.5-50 mg/kg).

Gerhart and Carlson demonstrated that >300 ug/kg benzo(a)pyrene (B(a)P), a known carcinogen and MFO inducer, is needed to induce MFO enzymes in sexually immature rainbow trout (30-50 g, 10 degrees C). Waste crankcase oil contains 0.0015% B(a)P. The highest concentrations given in our dose-response study was 150 ul (124.2 mg) of oil, which represents 1.9 ug of B(a)P per 10 to 70 g fish. In the present study the concentration of B(a)P administered was 27 to 190 ug/kg, which is 1.6 to 11 times lower than the above study. Therefore, it would appear that in this complex mixture of chemicals, even though synergistic and antagonistic effects must be taking place, they can be viewed as canceling one another (relative to the effect of B(a)P and neglecting other variables).

Tis.Wildlife: Terrestrial and Aquatic Wildlife, Domestic Animals and all Birds Whether Aquatic or not:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Wildlife, Domestic Animals, or Birds:

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound and III entries for summaries of information on individual components of this mixture.

B) Concentrations or Doses of Concern in Food Items Eaten by Wildlife, Birds, or Domestic Animals (Includes LD50 Values Which do not Fit Well into Other Categories, Includes Oral Doses Administered in Laboratory Experiments):

Lead is found in used motor oil and some forms of gasoline. Cattle & calves are often poisoned by ingesting crankcase oil drained from internal combustion engines. The farm dump is often a smorgasbord of poisons for animals that gain access to it [366, Booth, N.H., L.E. McDonald (eds.). Veterinary Pharmacology and Therapeutics. 5th ed. Ames, Iowa: Iowa State University Press, 1982. 1005].

Information from RTECS [607]:

LD50/LC50 - LETHAL DOSE/CONC 50% KILL
RAT: LD50; ROUTE: Oral; DOSE: 22500 mg/kg;
REFERENCE: Acute Toxicity Data. Journal of the American College of Toxicology, Part B 1:147, 1990.

C) Body Burden Residues in Wildlife, Birds, or Domestic Animals: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound and III entries for summaries of information on individual components of this mixture.

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound and III entries for summaries of information on individual components of this mixture.

B) Concentrations or Doses of Concern in Food Items

Eaten by Humans (Includes Allowable Tolerances in Human Food, FDA, State and Standards of Other Countries):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound and III entries for summaries of information on individual components of this mixture.

C) Body Burden Residues in Humans: Typical, Elevated, or of Concern Related to the Well-being of Humans:

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound and III entries for summaries of information on individual components of this mixture.

Tis.Misc. (Other Tissue Information):

Factors to consider when interpreting residues of petroleum hydrocarbons in wildlife tissues were summarized by Hall and Coon in 1988 [128].

Bio.Detail: Detailed Information on Bioconcentration, Biomagnification, or Bioavailability:

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound and III entries for summaries of information on individual components of this mixture.

Interactions:

It would appear that in the complex mixture of chemicals which make up used motor oil, even though synergistic and antagonistic effects must be taking place, they can be viewed as canceling one another (relative to the effect of B(a)P and neglecting other variables) [519]

Above text reprinted with permission from Environmental Toxicology and Chemistry, Volume 12(11), C. Upshall, J.F. Payne, and J. Hellou, "Induction of MFO Enzymes and Production of Bile Metabolites in Rainbow Trout (*Oncorhynchus mykiss*) Exposed to Waste Crankcase Oil." Copyright 1993 SETAC]. See above Tis.Fish section.

Uses/Sources:

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound and III entries for summaries of information on individual components of this mixture.

Forms/Preparations/Formulations:

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound and III entries for summaries of information on individual components of this mixture.

Chem.Detail: Detailed Information on Chemical/Physical Properties:

Caution: Every individual petroleum product has a unique "fingerprint," or distinct set of constituents most commonly identified by a gas chromatograph analysis. Due to the varying properties of the same general category of a petroleum product (for example, each source and stage of a used motor oil has a unique gas chromatograph "fingerprint"), careful assessment of the toxicity, specific gravity, and other physical characteristics of each individual oil must be taken into consideration to determine the exact effects of the product on the environment. Therefore, the below comments on used motor oils are to be considered as representative, but not absolute values typical of every batch of the product with the same name.

Used motor oil is generally similar to new motor oil except for the addition of additional:

Metals including zinc, magnesium, barium, lead, aluminum, chromium, copper, iron, manganese, nickel, silicon, and tin [752,961].

Water, gasoline, antifreeze, and thermal or breakdown products of various hydrocarbons [961].

Since PAHs are important hazardous components of this product, risk assessments should include analyses of PAHs and alkyl PAHs utilizing the NOAA protocol expanded scan [828] or other rigorous GC\MS\SIM methods.

Aromatics are considered to be the most acutely toxic component of petroleum products, and are also associated with chronic and carcinogenic effects [770]. Aromatics are often distinguished by the number of rings they possess, which may range from one to five [770]. Lighter, mono-aromatics (one ring) compounds include benzene, toluene, ethylbenzene, and xylenes [771]. Aromatics with two or more rings are referred to as polyaromatic hydrocarbons (PAHs) [770]. Waste crankcase oil contains several toxic components including up to 30% aromatic hydrocarbons, with as much as 22 ppm benzo(a)pyrene (a PAH) [75]. In a recent Upshall et al (1993) study, used motor oil had a density of 0.828 g/ml and contained 14% aromatics and 65.4% aliphatics (by weight) [519]. In this study, the sum of 26 individual PAHs represented 0.17% of the oil, or 1.2% of the aromatic fraction [519].

Above text reprinted with permission from Environmental Toxicology and Chemistry, Volume 12(11), C. Upshall, J.F. Payne, and J. Hellou, "Induction of MFO Enzymes and Production of Bile Metabolites in Rainbow Trout (*Oncorhynchus mykiss*) Exposed to Waste Crankcase Oil." Copyright 1993 SETAC]. Used motor oil typically has much higher concentrations of PAHs than new motor oil [40,519].

Additional detail on polycyclic aromatic compounds in one sample (one particular study, other samples would be different) of used engine oil [519, Reprinted with permission from Environmental Toxicology and Chemistry, Volume 12(11), C. Upshall, J.F. Payne, and J. Hellou, "Induction of MFO Enzymes and Production of Bile Metabolites in Rainbow Trout (*Oncorhynchus mykiss*) Exposed to Waste Crankcase Oil." Copyright 1993 SETAC]:

Compound	Concn. (ppm)
Low-molecular-weight PAHs	
Naphthalene	52.0
Acenaphthylene	1.5
Acenaphthene	3.7
Fluorene	67.0
Phenanthrene	200.0
Anthracene	22.0
High-molecular-weight PAHs	
Fluoranthene	55.0
Pyrene	120.0
Benz[a]anthracene	38.0
Chrysene	45.0
Benzofluoranthenes	46.0
Benzo(e)pyrene	32.0
Benzo(a)pyrene	15.0
Perylene	1.1
Indo(1,2,3-cd)pyrene	14.0
Dibenz(ah)anthracene	1.5
Benzo(ghi)perylene	72.0
High-molecular-weight PACs	
Dibenzothiophene	1.9
Alkylated PAHs	
Naphthalenes	
C-1 naphthalene	31.0
C-2 naphthalene	60.0
C-3 naphthalene	80.0
C-4 naphthalene	52.0
Phenanthrenes	
C-1 phenanthrene	300.0
C-2 phenanthrene	300.0
C-3 phenanthrene	140.0
C-4 phenanthrene	35.0

Pyrene, a polynuclear aromatic, has been found in used motor oil in concentrations ranging from 10.7 to 743 mg/kg [366].

Note: As mentioned in the Brief Introduction above, the concentration of some PAHs is much higher in used oil than in lubricating oil [519]. For example, Grimmer et al. reported concentrations of dibenz(a,c)-anthracene, 4-methylpyrene, fluoranthene, benz(a)anthracene, benzo(e)pyrene, benzo(g,h,i)perylene, and benzo(a)pyrene, respectively, 36, 49, 253, 720, 1,112, 4,770, and 7,226 times higher in "used" compared to "fresh" oil. The 4- to 7-ring PAHs have been especially implicated in the carcinogenic effect of used oil [519, Reprinted with permission from Environmental Toxicology and Chemistry, Volume 12(11), C. Upshall, J.F. Payne, and J. Hellou, "Induction of MFO Enzymes and Production of Bile Metabolites in Rainbow Trout (*Oncorhynchus mykiss*) Exposed to Waste Crankcase Oil." Copyright 1993 SETAC].

Additional Physicochemical information from Environment Canada [560]:

NOTE: In this section, for properties with more than one value, each value came from its own source; in other words, if API Gravity at 60 F was measured several times and several different answers were obtained, all of the answers are provided [560]:

API GRAVITY (60/60 degrees F)

NOTE: Created by the American Petroleum Institute (API), API gravity is an arbitrary scale expressing the gravity or density of liquid petroleum products [637]. This scale was created in order to compare the densities of various oils. $API\ gravity = (141.5 / \text{specific gravity [60/60 degrees F]}) - 131.5$, where specific gravity [60/60 degrees F] is the oil density at 60 degrees F divided by the density of water at 60 degrees F.

28.3

DENSITY (g/mL)

For temperatures of oil (T) between 0 and 30 C:
Density = $0.97871 - 0.000710 T$

NOTE: The densities of crude oils and oil products are dependent on the temperature and degree of weathering. The following density values are at "0% Weathering Volume" - in other words, fresh used motor oil.

Temp(C) Density (at 0% Weathering Volume)

0	0.8945
15	0.8848
15.6	0.906

SOLUBILITY

Aqueous Solubility (mg/L): The solubility of oil in water can be determined by bringing to equilibrium a volume of oil and water, and then analyzing the water phase. Oil's aqueous solubility is expressed as the cumulative concentration of the individually dissolved components. Solubility is significantly reduced by weathering.

	Temp not reported	22 C
Fresh Water	19.1	0.6
Seawater	12.83	

HYDROCARBON GROUP

NOTE: The main constituents of oil are generally grouped into the below categories. Asphaltene content increases with increasing weathering, as does wax content.

Hydrocarbon Group Analysis (Weight %):

Saturates	86.3
	76.6
Aromatics	12.9
	4.1
Polars	0.8
	3.8
Asphaltenes	0
Volatiles	3.2

METAL CONTENT

Other Metals (ppm):

Aluminum	15
Copper	18
Iron	220
Lead	18500
Silicon	17
Antimony	6
Sodium	59
Calcium	688
Barium	177
Zinc	1360
Magnesium	410

NON-METAL CONTENT [560]:

Nitrogen (Weight %):
0.090

Sulphur (Weight %):
0.29
0.54

VISCOSITY

NOTE: The viscosities of crude oils and oil products are dependent on the temperature and degree of weathering. The following viscosity values are at "0% Weathering Volume" - in other words, fresh used motor oil.

Dynamic Viscosity (mPa.s or cP):

Temp(C)	Dynamic Viscosity (at 0% Weathering Volume)
0	452.1
15	175.2

Kinematic Viscosity (mm²/sec or cSt):

Temp(C)	Kinematic Viscosity (at 0% Weathering Volume)
0	505.4
15	198.0
37.8	29.0
99	6.09

Pour Point (degrees C):

Pour point is the lowest temperature at which an oil sample is observed to flow when cooled under prescribed conditions. It is affected by weathering.

-36

INTERFACIAL TENSIONS

NOTE: Interfacial tension is the force of attraction between molecules at the interface of a liquid. These tensions are essential for calculating the spreading rates and the likely extent to which the oil will form oil-in-water and water-in-oil emulsions. The interfacial tensions of crude oils and oil products are dependent on the temperature and degree of weathering. The following tension values are at "0% Weathering Volume" - in other words, fresh used motor oil.

Air-Oil (mN/M or dynes/cm):

Temp(C)	Air-Oil Tension (at 0% Weathering Volume)
0	31.6
15	31.0

Oil-Seawater (mN/M or dynes/cm):

Temp(C)	Oil-Seawater Tension (at 0% Weathering Volume)
0	24.2

15 21.0

Oil-Water (mN/M or dynes/cm):

Temp(C)	Oil-Water (at 0% Weathering Volume)
0	27.1
15	24.4

EMULSION

NOTE: Water-in-oil emulsions are stable emulsions of small droplets of water incorporated in oil. Termed "chocolate mousse," these stable water-in-oil emulsions can have different characteristics than the parent crude oil. Emulsion characteristics of crude oils and oil products are dependent on the temperature and degree of weathering. The following typical values are at "0% Weathering Volume" - in other words, fresh used motor oil. In general, used motor oil is likely to form emulsions.

Emulsion Formation Tendency (in the VERY LIKELY range):

Temp(C)	Fraction of oil that forms an emulsion (f initial)
0	1.0
15	1.0

Emulsion Stability (in the VERY STABLE range):

Temp(C)	Fraction of oil in the emulsion that remains after settling (f final)
0	1.0
15	0.7

Water Content of Emulsion (volume %):

Temp(C)	Water Content (at 0% Weathering Volume)
0	57.9
15	72.8

DISPERSIBILITY

Chemical Dispersibility (% Dispersed):

Dispersant	Dispersibility
C 9527	33
CRX-8	31
ENER 700	36
Dasic	29

Natural Dispersibility (% Dispersed):

Temp(C)	Naturally Dispersed
15	17

FIRE AND REACTIVITY

Flash Point (C):
58.5

Fate.Detail: Detailed Information on Fate, Transport, Persistence, and/or Pathways:

Waste crankcase oils spilled on soil migrate downward by gravity through soil and possibly to groundwater, and spread laterally due to capillary forces and soil heterogeneity. The more water-soluble, lower molecular weight fractions tend to migrate faster than the less soluble, higher molecular weight fractions. The concentrations of constituents of waste crankcase oils decline in soil and groundwater with distance from the spill source because of adsorption by soil, biodegradation, and dilution [752].

Based on information regarding entry and fate, the following four scenarios by which waste crankcase oils (WCOs) enter the Canadian environment are of concern (percentages reported are 1990 estimates for automotive sector only) [752]:

- (i) re-refining (50.6%)
- (ii) burning as fuel (33.6%)
- (iii) road-oiling for dust suppression (3.0%); and
- (iv) land disposal (2.8%)

These scenarios were deemed to be of concern because they involved direct releases to the environment (dust suppression and land disposal) or the volumes involved were large (fuel and re-refining). Volumes of individual spills are usually small. Environment Canada (1993b) reported 35 spill events of WCOs from 1981 to 1992 which ranged from < 1 liter to 2273 liters [752]. Oil pollution from runoff, sewage discharges, and landfill leachates is a chronic environmental problem and a major factor in the degradation of global marine ecosystems. Chronic exposures may actually be more detrimental to marine ecosystems than the more dramatic oil spills, because organisms can bioaccumulate oil even at low concentrations [762].

The fate of WCOs in the environment is governed to a large extent by the entry scenario that lead to its release. Constituents of waste crankcase oils applied to road surfaces enter the surrounding environment by volatilization to air; transport of windborne dust to air and subsequent transfer to land and water; and runoff to adjacent soil or drainage ditches and eventually to local water systems. Burning waste crankcase oil leads to air emissions of metals and polycyclic aromatic hydrocarbons (PAHs) that are generally adsorbed to particulate matter and deposited to soil and water. After a spill to water, organic compounds with high vapor pressures (toluene, benzene) are volatilized to the atmosphere, while semi-volatile compounds (benzo(a)pyrene, naphthalene) and metals partition to the water or sediment phase [752].

In contrast to metals, most organic compounds (99.4 to 99.9%) in WCOs are destroyed during combustion in commercial boiler systems. Under certain circumstances, however, detectable levels of polychlorinated dibenzofuran and polychlorinated dibenzodioxin compounds can be formed during the combustion of WCOs. Photodegradation half-lives for several PAHs that could potentially be emitted from stacks, including fluorene, naphthalene, acenaphthene, anthracene, benzo(a)pyrene, phenanthrene, and pyrene, range from 0.37 hours to 550 days based on single substance experiments conducted under laboratory conditions. Mixtures of PAHs and particulate-bound PAHs are more resistant to photodegradation, particularly in the presence of other organic compounds. Limited data are available concerning the fate of non-metallic inorganic substances such as sulphur, nitrogen, phosphorus, and halogens that are emitted to the atmosphere following combustion of WCOs [752].

Laboratory and/or Field Analyses:

The major components of used motor oil consist of aliphatic and aromatic hydrocarbons (such as phenol, naphthalene, benz(a)anthracene, benzo(a)pyrene, and fluoranthene) [752]. Waste crankcase oil contains several toxic components including up to 30% aromatic hydrocarbons, with as much as 22 ppm benzo(a)pyrene (a PAH) [75]. See also: PAHs as a group entry.

In a recent Upshall et al (1993) study, used motor oil used in the investigation had a density of 0.828 g/ml and contained 14% aromatics and 65.4% aliphatics (by weight) [519]. In this study, the sum of 26 individual PAHs represented 0.17% of the oil, or 1.2% of the aromatic fraction [519, Reprinted with permission from Environmental Toxicology and Chemistry, Volume 12(11), C. Upshall, J.F. Payne, and J. Hellou, "Induction of MFO Enzymes and Production of Bile Metabolites in Rainbow Trout (*Oncorhynchus mykiss*) Exposed to Waste Crankcase Oil." Copyright 1993 SETAC]. Used motor oil typically has much higher concentrations of PAHs than new motor oil [40,519].

Since metals are a concern with used motor oil (see Chem.Detail Section,) an ICP scan for a general suite of metals should supplement organic analyses.

Recent (1991) studies have indicated that EPA approved methods used for oil spill assessments (including total petroleum hydrocarbons method 418.1, semivolatle priority pollutant organics methods 625 and 8270, and volatile organic priority pollutant methods 602, 1624, and 8240) are all inadequate for generating scientifically defensible information for Natural Resource Damage Assessments [468]. These general organic chemical methods are deficient in chemical selectivity (types of constituents analyzed) and sensitivity (detection limits); the deficiencies in these two areas lead to an inability to interpret the environmental significance of the data in a scientifically defensible manner [468]. A great deal of uncertainty remains in the use of dose-response relationships based on crude oil as a whole mixture [734].

The relative proportions of hazardous compound constituents

present in petroleum-based oil contamination is typically quite variable. The lab analyses most appropriate for measuring different types of oil contamination depend upon the type of oil involved and the reason for measuring the contamination. The farther one progresses from lighter towards heavier oils (the general progression from light towards heavy is the following: Diesel, No. 2 Fuel Oil, Light Crudes, Medium Crude Oils, Heavy Crudes, No. 6 Fuel Oil, etc.) the greater the percentage of PAHs and other semi-volatiles (many of which are not so immediately toxic as the volatiles but which can result in long term/chronic impacts). These heavier oils thus need to be analyzed for the semi volatile compounds which typically pose the greatest long term risk, PAHs and (especially) alkylated PAHs.

Crude oil consists of thousands of individual compounds. The major groups include the saturated alkanes, alkenes, benzene, alkylated and aryl benzenes, polynuclear aromatics, heterocyclic aromatics, and hetro-atom substituted alkanes, alkenes and aromatics [783]. Some of the more toxic compound classes are: low molecular weight aromatics (such as benzene, toluene, xylene, other monocyclic aromatics), and polynuclear aromatic hydrocarbons (PAH) [713, 745]. Due to the presence of light aromatics and PAHs in fuel crude oil, we recommend the following decision tree:

Decision Tree (dichotomous key) for selection of lab methods for measuring contamination from midrange to heavy crude oils, number 6 and heavier fuel oils, bunker C, used motor oils, and all other oils considered to be heavy):

- 1a. Your main concern is biological effects of petroleum products.....2
- 1b. Your main concern is cleanup or remediation but no ecological or human resources are at risk.....3
- 2a. The resource at risk is primarily humans via a drinking water pathway, either the contamination of groundwater used for drinking water, or the fresh* or continuing contamination of surface waters used as drinking water, or the risk is primarily to aquatic species in confined** surface waters from a fresh* spill, or the risk is to surface waters re-emerging from contaminated groundwater resources whether the spill is fresh* or not; the medium and/or pathway of concern is water rather than sediments, soil, or tissues. Note: although heavy products have a lower percentage of BTEX and other relatively soluble compounds which typically threaten drinking water, ground water, or water column organisms, some heavy oils including crudes do contain some of these water soluble compounds, so they cannot be ignored.....4
- 2b. The resource at risk is something else.....5
- 3a. The spilled substance is a fresh* oil product of known composition: If required to do so by a regulatory authority, perform whichever Total Petroleum Hydrocarbon (TPH) analysis

specified by the regulator. However, keep in mind that due to its numerous limitations, the use of the common EPA method 418.1 for Total Petroleum Hydrocarbons is not recommended as a stand-alone method unless the results can first be consistently correlated (over time, as the oil ages) with the better NOAA protocol expanded scan*** for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs. If not required to perform an EPA method 418.1-based analysis for TPH, instead perform a Gas Chromatography/Flame Ionization Detection (GC/FID) analysis for TPH using the spilled substance as a calibration standard. GC/FID methods can be sufficient for screening purposes when the oil contamination is fresh*, unweathered oil and when one is fairly sure of the source [657]. If diesel 1D was spilled, perform TPH-D (1D) using California LUFT manual methods (typically a modified EPA method 8015) [465] or a locally available GC/FID method of equal utility for the product spilled. However, no matter which TPH method is used, whether based on various GC/FID or EPA method 418.1 protocols, the investigator should keep in mind that the effectiveness of the method typically changes as oil ages, that false positives or false negatives are possible, and that the better Gas Chromatography-Mass Spectrometry-Selected Ion Mode (GC/MS/SIM) scans (such as the NOAA expanded scan***) should probably be performed at the end of remediation to be sure that the contamination has truly been cleaned up. Another option for fresh oil: in cases where an inexpensive screening scan is desired, consider using an HPLC/Fluorescence scan method for sediment or bile metabolite samples. Such scans are available from laboratories at Texas A. and M., Arthur D. Little, and the NOAA lab in Seattle. This scan is not much more expensive, and less prone to false negatives and various other problems than some of the more common screening methods (TPH-EPA 418.1 and Oil and Grease). Screening measures the total fluorescence of oil components while GC/MS measures individual aromatic compounds [521]. Thus, HPLC/fluorescence screening allowed detecting lower concentrations of petroleum-related aromatic compounds in samples contaminated by Prudhoe Bay Crude Oil than did analysis by GC/MS [521].

3b. The spilled product is not fresh* or the contamination is of unknown or mixed composition.....6

4. Analyze for Benzene, Toluene, Ethyl Benzene, and Toluene (BTEX) compounds in water as part of a broader scan of volatiles using EPA GC/MS method 8260 (8260 is replacing 8240 [1013]). The standard EPA GC/MS method 8260 protocol will be sufficient for some applications, but the standard EPA method 8240 (and especially the less rigorous EPA BTEX methods such as method 8020 for soil and method 602 for water) are all inadequate for generating scientifically defensible information for Natural Resource Damage Assessments [468]. The standard EPA methods are also inadequate for risk assessment purposes. Thus, when collecting information for

possible use in a Natural Resource Damage Assessment or risk assessment, it is best to ask the lab to analyze for BTEX compounds and other volatile oil compounds using a modified EPA GC/MS method 8260 (8260 is replacing 8240 [1013]) method using the lowest possible Selected Ion Mode detection limits and increasing the analyte list to include as many alkyl BTEX compounds as possible. Also analyze surface or (if applicable) ground water samples for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs using the NOAA protocol expanded scan*** modified for water samples using methylene chloride extraction. If the contaminated water is groundwater, before the groundwater is determined to be remediated, also analyze some contaminated sub-surface soils in contact with the groundwater for BTEX compounds (EPA GC/MS method 8260 (8260 is replacing 8240 [1013])), and PAHs (NOAA protocol expanded scan***). The magnitude of any residual soil contamination will provide insight about the likelihood of recontamination of groundwater resources through equilibria partitioning mechanisms moving contamination from soil to water.

- 5a. The medium of concern is sediments or soils.....6
- 5b. The medium of concern is biological tissues.....7
- 6. Perform the NOAA protocol expanded scan*** for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs. If there is any reason to suspect fresh* or continuing contamination of soils or sediments with lighter volatile compounds, also perform EPA GC/MS method 8260 using the lowest possible Selected Ion Mode (SIM) detection limits and increasing the analyte list to include as many alkyl Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) compounds as possible.
- 7a. The problem is direct coating (oiling) of wildlife or plants with spilled oil product.....8
- 7b. The problem is something else.....9
- 8. Perform NOAA protocol expanded scan*** for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs and/or GC/FID fingerprinting of the coating oil only if necessary to identify the source or exact oil. If the source is known and no confirmation lab studies are necessary: dispense with additional chemical laboratory analyses and instead document direct effects of coating: lethality, blinding, decreased reproduction from eggshell coating, etc., and begin cleaning activities if deemed potentially productive after consultations with the Fish and Wildlife Agencies.
- 9a. The concern is for impacts on water column organisms (such as fish or plankton).....10
- 9b. The concern is for something else (including benthic

10. If exposure to fish is suspected, an HPLC/Fluorescence scan for polycyclic aromatic hydrocarbon (PAH) metabolites in bile may be performed to confirm exposure [844]. The HPLC/fluorescence scan looks for the presence of metabolites of PAHs: naphthalene, phenanthrene, and benzo[a]pyrene. The technique does not identify or quantify actual PAH compounds, but subsequent gas chromatography analyses can be done to confirm the initial findings. Even the semi-quantitative Total Scanning Fluorescence (TSF) done inexpensively by labs such as GERG are a better measure of PAH contamination than GC/FID, which measures less persistent and less hazardous aliphatics. For bottom-dwelling fish such as flounders or catfish, also analyze the bottom sediments (see Step 6 above). Fish which spend most of their time free-swimming above the bottom in the water column can often avoid toxicity from toxic petroleum compounds in the water column, but if fish are expiring in a confined** habitat (small pond, etc.), EPA GC/MS method 8260 (8260 is replacing 8240 [1013]) and the NOAA protocol expanded scan*** for PAHs could be performed to see if Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX), naphthalene, and other potentially toxic compounds are above known acute toxicity benchmark concentrations. Zooplankton populations impacted by oil usually recover fairly quickly unless they are impacted in very confined** or shallow environments [835] and the above BTEX and PAH water methods are often recommended rather than direct analyses of zooplankton tissues.
- 11a. The concern is for benthic invertebrates: analyze invertebrate whole-body tissue samples and surrounding sediment samples for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs using the NOAA protocol expanded scan***. If the spill is fresh* or the source continuous, risk assessment needs may also require that the sediments which form the habitat for benthic invertebrates be analyzed for Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) and other volatile compounds using EPA GC/MS method 8260 (8260 is replacing 8240 [1013]) or modified EPA method 8260 in the Selected Ion Mode (SIM). Bivalve invertebrates such as clams and mussels do not break down PAHs as well or as quickly as do fish or many wildlife species. They are also less mobile. Thus, bivalve tissues are more often directly analyzed for PAH residues than are the tissues of fish or wildlife.
- 11b. The concern is for plants or for vertebrate wildlife including birds, mammals, reptiles, and amphibians: polycyclic aromatic hydrocarbons (PAHs) and other petroleum hydrocarbons break down fairly rapidly in many wildlife groups and tissues are not usually analyzed directly. Instead direct effects are investigated and water, soil, sediment, and food items encountered by wildlife are usually analyzed for PAHs and alkyl PAHs using the NOAA protocol expanded scan***. If the

spill is fresh* or the source continuous, risk assessment needs may also require that these habitat media also be analyzed for Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) and other volatile compounds using EPA GC/MS method 8260 (8260 is replacing 8240 [1013]) or modified EPA method 8260 in the Selected Ion Mode (SIM). Less is known about plant effects. However, the same methods recommended above for the analyses of water (Step 4 above) and for sediments or soils (Step 6 above) are usually also recommended for these same media in plant or wildlife habitats. If wildlife or plants are covered with oil, see also Step 8 (above) regarding oiling issues.

* Discussion of the significance of the word "fresh": The word "fresh" cannot be universally defined because oil breaks down faster in some environments than in others. In a hot, windy, sunny, oil-microbe-rich, environment in the tropics, some of the lighter and more volatile compounds (such as the Benzene, Toluene, Ethyl Benzene, and Xylene compounds) would be expected to disappear faster by evaporation into the environment and by biodegradation than in a cold, no-wind, cloudy, oil-microbe-poor environment in the arctic. In certain habitats, BTEX and other relatively water soluble compounds will tend to move to groundwater and/or subsurface soils (where degradation rates are typically slower than in a sunny well aerated surface environment). Thus, the judgement about whether or not oil contamination would be considered "fresh" is a professional judgement based on a continuum of possible scenarios. The closer in time to the original spill of non-degraded petroleum product, the greater degree the source is continuous rather than the result of a one-time event, and the more factors are present which would retard oil evaporation or breakdown (cold, no-wind, cloudy, oil-microbe-poor conditions, etc.) the more likely it would be that in the professional judgement experts the oil would be considered "fresh." In other words, the degree of freshness is a continuum which depends on the specific product spilled and the specific habitat impacted. Except for groundwater resources (where the breakdown can be much slower), the fresher the middle distillate oil contamination is, the more one has to be concerned about potential impacts of BTEX compounds, and other lighter and more volatile petroleum compounds.

To assist the reader in making decisions based on the continuum of possible degrees of freshness, the following generalizations are provided: Some of the lightest middle distillates (such as Jet Fuels, Diesel, No. 2 Fuel Oil) are moderately volatile and soluble and up to two-thirds of the spill amount could disappear from surface waters after a few days [771,835]. Even heavier petroleum substances, such as medium oils and most crude oils will evaporate about one third of the product spilled within 24 hours [771]. Typically the volatile fractions disappear mostly by evaporating into the atmosphere. However, in some cases, certain water soluble fractions of oil including Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) compounds move down into groundwater. BTEX compounds are included in the more volatile and water soluble fractions, and

BTEX compounds as well as the lighter alkanes are broken down more quickly by microbes than heavier semi-volatiles such as alkyl PAHs and some of the heavier and more complex aliphatic compounds. Thus after a week, or in some cases, after a few days, there is less reason to analyze surface waters for BTEX or other volatile compounds, and such analyses should be reserved more for potentially contaminated groundwaters. In the same manner, as the product ages, there is typically less reason to analyze for alkanes using GC/FID techniques or TPH using EPA 418.1 methods, and more reason to analyze for the more persistent alkyl PAHs using the NOAA protocol expanded scan***.

** Discussion of the significance of the word "confined": Like the word "fresh" the word "confined" is difficult to define precisely as there is a continuum of various degrees to which a habitat would be considered "confined" versus "open." However, if one is concerned about the well-being of ecological resources such as fish which spend most of their time swimming freely above the bottom, it makes more sense to spend a smaller proportion of analytical funding for water column and surface water analyses of Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) and other volatile or acutely toxic compounds if the spill is in open and/or deep waters rather than shallow or "confined" waters. This is because much of the oil tends to stay with a surface slick or becomes tied up in subsurface tar balls. The petroleum compounds which do pass through the water column often tend to do so in small concentrations and/or for short periods of time, and fish and other pelagic or generally mobile species can often swim away to avoid impacts from spilled oil in "open waters." Thus in many large oil spills in open or deep waters, it has often been difficult or impossible to attribute significant impacts to fish or other pelagic or strong swimming mobile species in open waters. Lethality has most often been associated with heavy exposure of juvenile fish to large amounts of oil products moving rapidly into shallow or confined waters [835]. Different fish species vary in their sensitivity to oil [835]. However, the bottom line is that in past ecological assessments of spills, often too much money has been spent on water column analyses in open water settings, when the majority of significant impacts tended to be concentrated in other habitats, such as benthic, shoreline, and surface microlayer habitats.

*** The expanded scan protocols for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs have been published by NOAA [828].

End of Key.

Contaminants data from different labs, different states, and different agencies, collected by different people, are often not very comparable (see also, discussion in the disclaimer section at the top of this entry).

As of 1997, the problem of lack of data comparability (not only for water methods but also for soil, sediment, and tissue

methods) between different "standard methods" recommended by different agencies seemed to be getting worse, if anything, rather than better. The trend in quality assurance seemed to be for various agencies, including the EPA and others, to insist on quality assurance plans for each project. In addition to quality control steps (blanks, duplicates, spikes, etc.), these quality assurance plans call for a step of insuring data comparability [1015,1017]. However, the data comparability step is often not given sufficient consideration. The tendency of agency guidance (such as EPA SW-846 methods and some other new EPA methods for bio-concentratable substances) to allow more and more flexibility to select options at various points along the way, makes it harder to insure data comparability or method validity. Even volunteer monitoring programs are now strongly encouraged to develop and use quality assurance project plans [1015,1017].

At minimum, before using contaminants data from diverse sources, one should determine that field collection methods, detection limits, and lab quality control techniques were acceptable and comparable. The goal is that the analysis in the concentration range of the comparison benchmark concentration should be very precise and accurate.

It should be kept in mind that quality control field and lab blanks and duplicates will not help in the data quality assurance goal as well as intended if one is using a method prone to false negatives. Methods may be prone to false negatives due to the use of detection limits that are too high, the loss of contaminants through inappropriate handling, or the use of inappropriate methods. The use of inappropriate methods is particularly common related to oil products.

Other Notes:

Although EPA method 418.1: Petroleum Hydrocarbons expressed as Total Petroleum Hydrocarbons (TPH), is recommended by many State agencies, some consulting firms, and some laboratories for certain regulatory and screening applications (often leaking underground storage tanks), this method is not well suited to crude oil contamination or to the more persistent hazardous constituents in oil. Low values tend to give the mistaken impression that a site is clean when it really isn't (a false negative). For example, a field test of bioremediation of soils contaminated with Bunker C (a heavy fuel) at a refinery in Beaumont, Texas, utilized oil and grease data, which (although the data was quite variable) seemed to indicate bioremediation was taking place [728]. A comparison of the oil and grease data at this site with TPH data at this site suggested the same thing, that the data was quite variable but if anything, the oil was being slowly being cleaned up by bioremediation (Bruce Herbert, Texas A. and M., Department of Geology, personal communication, 1995). However, a later study of the same site utilizing the expanded scan for PAHs [828] (a modified EPA 8270 including alkyl homologues and lower detection limits), indicated that very little bioremediation of hazardous alkyl PAHs and multi-ring PAHs was actually taking place [727]. Thus, utilizing either oil and grease or TPH analyses would tend to

lead one to the faulty conclusion that the harmful compounds were being naturally cleaned up at an acceptable rate. This is partly because the TPH and oil and grease methods tend to favor the lighter and less alkylated PAHs, whereas many of the carcinogenic and longer lasting PAHs are the heavier multi-ringed and alkylated compounds.

In cases where a less expensive screening scan is desired, consider using an HPLC/Fluorescence scan method for sediment or bile metabolite samples. Such scans are available from laboratories at Texas A. and M., Arthur D. Little, and the NOAA lab in Seattle. This scan is less prone to false negatives and various other problems than some of the more common screening methods (TPH-EPA 418.1 and Oil and Grease). HPLC/Fluorescence is less expensive than some of the more rigorous scans. The HPLC/fluorescence scan can be used for analyses of fish bile: the scan looks at bile directly for the presence of metabolites of PAHs: naphthalene, phenanthrene, and benzo(a)pyrene. The technique does not identify or quantify actual PAH compounds, but subsequent gas chromatography analyses can be done to confirm the initial findings. Even the semi-quantitative Total Scanning Fluorescence (TSF) done inexpensively by labs such as GERG are a better measure of PAH contamination than GC/FID, which measures less persistent and less hazardous aliphatics.

TLC Patterns for Used Engine Oil [783]:

As an oil becomes used, it breaks down to give a wide variety of oxygenated and aromatic hydrocarbons. The thin-layer chromatography (TLC) pattern of used oil will resemble that of fresh oil with the added presence of these polar breakdown products. It will show a large oval spot at Rf 0.9 (hexane) visible with iodine staining and a thin streak stretching from Rf 0.9 to 0.0. Some heavy polynuclear aromatics (PNA) with an Rf 0.0 to 0.3 may be visible under the UV light. The ratio of the saturated hydrocarbons to the aromatic hydrocarbons will depend upon the degree to which the oil has been degraded.

Additional lab method methods are summarized by ATSDR [961].