USED OIL IN BUNKER FUEL:

A REVIEW OF POTENTIAL HUMAN HEALTH IMPLICATIONS

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EXECUTIVE SUMMARY

Used oil constitutes about one third of California's hazardous waste stream, with about 100 million gallons recovered and managed annually in the State. Given this large volume, the improper or illegal disposal of used oil can potentially lead to adverse effects on the environment and human health. The Used Oil Recycling Program in the California Integrated Waste Management Board (CIWMB) develops and promotes alternatives to the illegal disposal of used oil by establishing a Statewide network of collection opportunities and undertaking outreach efforts to inform and motivate the public to recycle used oil.

Volumes of used oil recycled in California have shown a steady increase over the years. The largest volume end-product of the recycling of California's used oil recycling is fuel oil, making up an average of about two-thirds of the volume of all recycled products annually from 1992 to 2002. Fuel oil is combusted for energy in a variety of applications, including asphalt plants, industrial boilers, electric utilities, steel mills, cement and lime kilns, pulp and paper mills, and commercial boilers. In addition, used oil-derived fuel oil has reportedly been blended into "bunker fuel" for ship engines (see diagram on page ix). The term *bunker fuel* is often used to refer to the fuel burned in oceangoing ships for propulsion, and mainly consists of residual fuel. Bunker fuel is also used for energy in power plants, cement kilns and other industrial facilities. (For definitions of used oil-derived products and other terms used in this report, see page viii.)

While 10 to 25 percent of all marine fuels sold on the West Coast had been blended with used oil in the past, this practice rarely occurs today. Since the mid-1990s, the shipping industry has become increasingly less inclined to accept bunker fuel containing used oil. There are a number of reasons for this: the potential for the used oil to contain contaminants that can seriously damage the ship's engine; evidence – albeit contentious -- that used oil itself can cause engine damage or affect engine performance; and, with the rising cost of fuel, an unwillingness to pay fuel oil prices for a waste product.

The Office of Environmental Health Hazard Assessment (OEHHA) has conducted research to investigate the potential human health effects associated with the combustion in marine engines of bunker fuel supplemented with used oil or used oil-derived fuels, compared with bunker fuel alone. Our research revealed a lack of sufficient analytical data with which to estimate the human health risks from the combustion of used oil in bunker fuel. (In this report, data on the constituents of used oil is presented, since we found no analytical data specifically on fuel oil derived from used oil; since only physical processes are employed in recycling used oil to fuel oil, both materials are likely to be similar in composition.) More specifically:

- Analytical data on the chemical constituents of used oil are mostly from the mid-1980s to mid-1990s, and were limited to a few select contaminants.

- Constituent data on marine fuels focused mainly on chemicals that can affect fuel performance or cause engine damage, rather than chemicals that can impact human health.

- The hazardous constituents in emissions from the combustion of marine fuels and of used oil are inadequately characterized for risk assessment purposes.

- Constituent-specific emissions factors needed to estimate airborne contaminant concentrations are also not available.

Nevertheless, it appears from the available data that the levels of certain hazardous constituents of concern – arsenic, cadmium, chromium, lead, and polycyclic aromatic hydrocarbons -- are within an order of magnitude when comparing used oil and residual fuel. Thus, addition of used oil to bunker fuel at the 1 to 3 percent dilution rates seen in the past would not result in substantially higher concentrations of these chemicals in the resultant fuel.

Industry-wide specifications being developed by the International Standards Organization will explicitly prohibit the presence of used oil in marine fuels. Furthermore, new international, federal and State regulations are likely to result in significant changes in the nature of marine fuels, particularly in allowable sulfur levels. These changes, in turn, have the potential to further restrict the addition of used oil into marine fuels.

Marine diesel oil (MDO), one of the products of used oil recycling, is very similar to the distillates commonly used in today's marine fuels. Its low sulfur, ash and viscosity make it highly desirable as a blending agent for bunker fuel. Forthcoming regulations that lower the allowable levels of sulfur in distillate fuel may preclude the use of MDO in the smaller vessels (such as harbor craft); however, the use of MDO as a blending agent with residual fuel is not likely to be affected by regulatory changes.

There is little information about the possible environmental and human health impacts resulting from burning fuel oils, including MDO, that are derived from used oil. Assessing the human health risks from the combustion of these fuels would require the same data that would be needed to assess the incremental risks from burning used oil in bunker fuel: chemical constituent data, emissions data, and emission factors specific to the fuel, constituent, and combustion device (see bullets above).

Since the marine market for fuel oil recycled from used oil is likely to continue to diminish, it would be worthwhile to examine other recycling options. One such option would be as feedstock in the petroleum refining process. The feasibility and potential environmental and human health impacts of this option could be evaluated.

DEFINITION OF TERMS USED IN THIS REPORT

Bunker fuel. A general term often used to refer to fuel burned in ships for propulsion; bunker fuel mainly consists of *residual fuel* blended with *distillate fuel*.

Distillate fuel. A general classification for one of the petroleum fractions produced in conventional distillation operations; includes *marine diesel oil* and *diesel fuels* (EIA, 2004b).

Fuel oil cutter. Fuel oil used as a blending agent for other fuels, such as to lower viscosity; a major product of the recycling of used oil.

Industrial oil. Any compressor, turbine or bearing oil, hydraulic oil, metalworking oil or refrigeration oil; does not include dielectric fluids (Public Resources Code 48616).

Lubricant base stock. The refined petroleum fraction into which additives are blended to produce finished lubricants (BP Lubricants, 2004).

Lubricating oil. Any oil intended for use in an internal combustion engine crankcase, transmission, gearbox, or differential in an automobile, bus, truck, vessel, plane, train, heavy equipment, or other machinery powered by an internal combustion engine (Public Resources Code 48618).

Marine diesel oil (MDO). A distillate fuel produced from crude oil, as well as from the re-refining of used oil.

Marine fuels. Distillate fuel, residual fuel or a blend of both, used to provide power for marine vessels.

Recycled oil. Any oil produced from used oil which has been prepared for reuse and which meets minimum standards of purity; includes re-refined oil and recycled fuel oil.

Recycling. Generally refers to using, reusing or reclaiming a recyclable material. For used oil, includes re-refining to lubricant base stock, or reprocessing to recycled fuel oil or other petroleum products. (Health and Safety Code 25121.1).

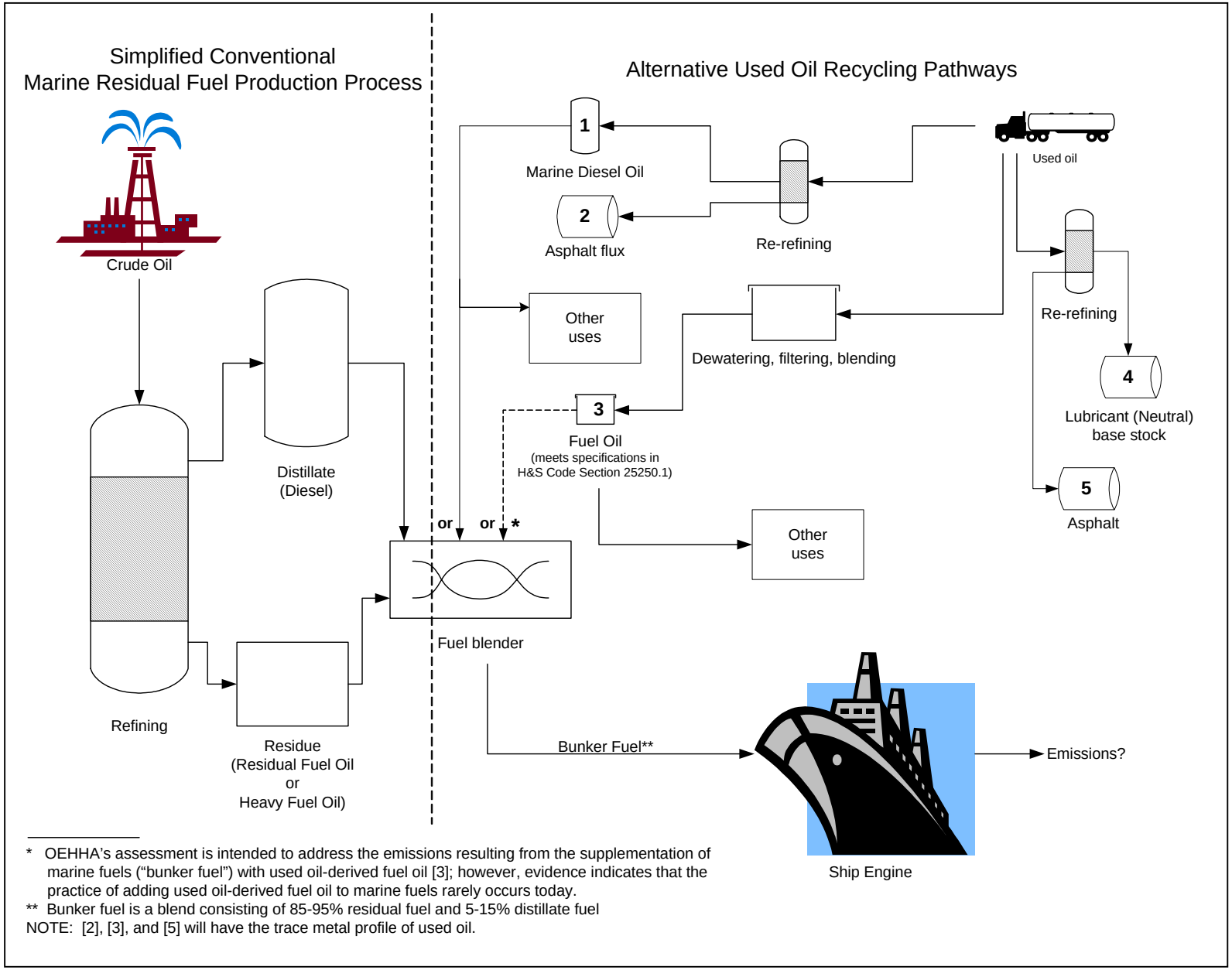
Re-refining. A process involving extensive physical and chemical treatment to yield a high quality *marine diesel oil* or *lubricant base stock* comparable to virgin lubrication oil product.

Reprocessing. A process involving chemical and physical treatment, including blending, to remove water or solid contaminants to yield a better fuel.

Residual fuel. A general classification for the heavier oils, known as No. 5 and No. 6 fuel oils, that remain after the distillate fuel oils and lighter hydrocarbons are distilled away in refinery operations. No. 6 fuel oil includes Bunker C fuel oil and is used for the production of electric power, for space heating, as marine vessel fuel, and for various industrial purposes (EIA, 2004b).

Used oil. Any oil that has been refined from crude oil, or any synthetic oil, that has been used, and, as a result of use or as a consequence of extended storage, or spillage, has been contaminated with physical or chemical impurities (Health and Safety Code 25250.1).

From Used Oil to Bunker Fuel



* OEHHA's assessment is intended to address the emissions resulting from the supplementation of marine fuels ("bunker fuel") with used oil-derived fuel oil [3]; however, evidence indicates that the practice of adding used oil-derived fuel oil to marine fuels rarely occurs today.

** Bunker fuel is a blend consisting of 85-95% residual fuel and 5-15% distillate fuel

NOTE: [2], [3], and [5] will have the trace metal profile of used oil.

1.0 INTRODUCTION

The Office of Environmental Health Hazard Assessment (OEHHA) has conducted an evaluation of the potential human health implications associated with the addition of used oil to bunker fuel that is combusted in marine vessels. The term bunker fuel is often used to refer to the fuel burned in oceangoing ships for propulsion, and mainly consists of residual fuel. This evaluation is provided to the California Integrated Waste Management Board's (CIWMB) Used Oil Recycling Program.

The CIWMB is charged with the implementation of a statewide Used Oil Recycling Program pursuant to the 1991 California Oil Recycling Enhancement Act (Public Resources Code Section 48601 *et seq*.). Under the Program, CIWMB assists in the establishment of a statewide network of collection opportunities, and conducts outreach efforts to inform and motivate the public to recycle used oil (CIWMB, 2004c). These activities support the need to properly manage used oil, given the adverse environmental and public health consequences of the improper or illegal disposal of used oil.

In compiling the information necessary to conduct a risk assessment, OEHHA also researched current practices by oil recyclers, fuel blenders and vessel operators relating to the production, blending and use of fuels derived from used oil. In this report, OEHHA discusses:

- The regulation and management of California used oil
- The fuels used in marine vessels, including the potential changes in industry practices, fuel specifications and regulations at the State, federal and international levels that may impact the recycled oil market; and
- The hazardous constituents in used oil, compared to those in bunker fuel, and the data gaps that preclude a full assessment of the potential health risks associated with exposures to contaminants in used oil.

2.0 USED OIL MANAGEMENT

With a growing world population and the continuing industrialization of developing nations, the demand for energy will continue to increase. Despite technological advancements in alternative fuels, the dominant energy source over the next several decades will continue to be petroleum. Worldwide petroleum consumption is projected to increase in the year 2020 to 119.6 million barrels per day, a 60 percent increase from 74.9 million barrels per day in 1999 (Committee on Oil in the Sea, 2003*)*. California likewise relies upon petroleum as its main energy source. From 1960 to 2000, the State's petroleum consumption almost doubled, with the transportation sector accounting for more than 80 percent of the State's petroleum consumption since 1991 (Energy Information Administration, 2000a; 2000b). In addition to increasing demand, the cost of petroleum is expected to continue to rise. Crude oil prices rose from $20 per barrel in the late 1990s to over $50 today (Energy Information Administration, 2000a, 2004c).

Used oil is a valuable resource because of its lubrication and heat value. While the volume of used oil managed annually in California represents a small amount (less than 0.5 percent) relative to the volume of petroleum products consumed in the State (over 27 billion gallons in the year 2000), it is nevertheless a feedstock in the production of lubricant base stock, fuel oil, distillates and other products.

2.1 Regulations governing used oil management

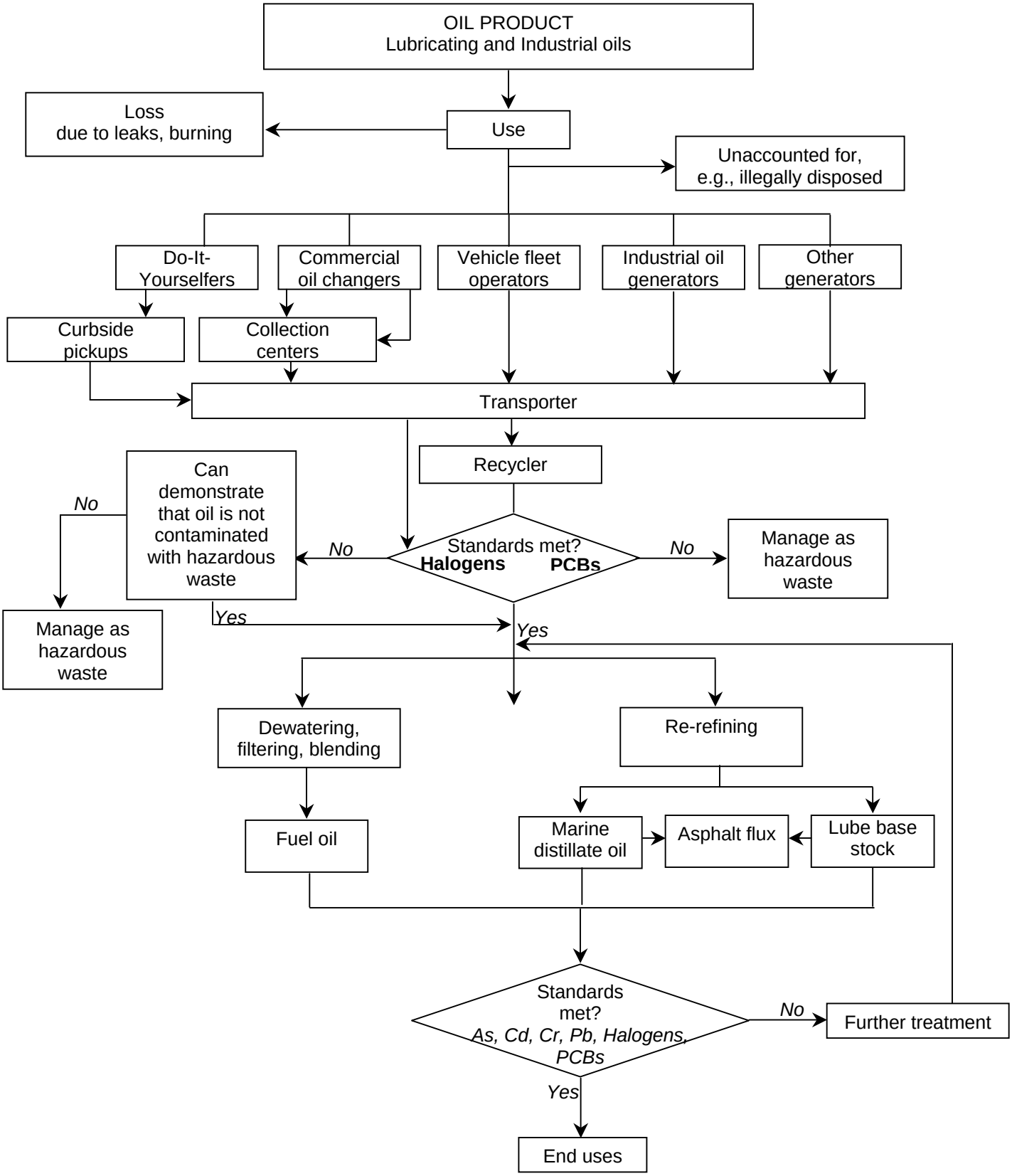
About 100 million gallons of used oil are recovered and managed in California annually, following their use in industrial applications and as lubricants (such as motor oil in engine crankcases). "Used oil" is defined as any oil that has been refined from crude oil, or any synthetic oil, that has been used and, as a result of use or as a consequence of extended storage or spillage, has been contaminated with physical or chemical impurities (Health and Safety Code Section 25250.1). Unlike the federal government, California regulates used oil as a hazardous waste. In spite of this status, used oil is subject to a separate set of management standards (both at the federal and State levels) intended to prevent the creation of barriers to recycling, while still protecting against potential adverse human and environmental health impacts from the mismanagement of used oil. Figure 1 illustrates the flow of used oil managed in California.

California law prohibits discharging used oil to sewers, drainage systems, surface water or groundwater, watercourses or marine waters; incineration or burning of used oil as fuel; depositing used oil on land; or using it as a dust suppressant or as an insect or weed control agent. Mixing of used oil with other hazardous wastes, such as solvents, antifreeze and fuels, is also prohibited.

The Department of Toxic Substances Control (DTSC) is responsible for the regulation of hazardous wastes in California. Under California law, the used oil management standards apply to used oil intended to be recycled. The used oil should not exhibit any hazardous characteristics (ignitability, corrosivity, toxicity and reactivity) that render a waste hazardous. In addition, used oil must not contain polychlorinated biphenyls (PCBs) at a concentration at or above 5 parts per million (ppm), or halogens (e.g., compounds containing chlorine, bromine, and fluorine) above 1,000 ppm. Used oil generators, collection centers, transporters, transfer facilities and recycling facilities are required to determine whether the total halogen content of each used oil shipment exceeds 1,000 ppm (Section 66279.10, Title 22, California Code of Regulations). Used oil containing more than 1,000 ppm halogens is presumed to be mixed with halogenated hazardous wastes and must be managed as such, unless the generator of the waste can demonstrate otherwise (Health and Safety Code Section 25250.1(a)(1)(B)(v) and Title 22, California Code of Regulations, Section 66279.10).

Unless specifically exempted by law, used oil can be transported only by a registered hazardous waste transporter. Shipments of used oil are accompanied by a standard hazardous waste manifest or a consolidated hazardous waste manifest that contains specified information. The transporter must take the shipment to an authorized used oil storage or treatment facility (DTSC, 2003).

Figure 1. Used Oil Flow in California



Facilities that recycle used oil must be authorized to do so by DTSC. These recycling facilities are required to test their end-products -- generally referred to as “recycled oil” -- prior to shipment to determine compliance with “purity standards” established for flashpoint, and limits for specified hazardous constituents. California (Health and Safety Code Section 25250.1(a)(3)(B)) and U.S. EPA specifications for these constituents are listed in Table 1.

Table 1. Specifications for Constituents in Recycled Oil

	California limits (ppm)	U.S. EPA limits (ppm)
Lead	50	100
Arsenic	5	5
Cadmium	2	2
Chromium	10	10
Halogens	3,000	4,000
Polychlorinated biphenyls	2	*

* The burning of used oil containing PCBs is regulated under Title 40, Code of Federal Regulations, Section 761.20(e).

Under federal regulations, used oil or fuel produced from used oil exceeding the limits set by the U.S. Environmental Protection Agency (U.S. EPA) can be burned for energy recovery only in industrial and utility boilers, industrial furnaces, hazardous waste incinerators, and used oil-fired space heaters that meet specified provisions (Title 40, Code of Federal Regulations, Section 279.11). In California, burning used oil in a space heater unit is not allowed; U.S. EPA allows the burning of used oil that is generated by the owner or operator of the unit or received from do-it-yourselfers in used oil-fired space heaters, provided that the heater has a maximum capacity not exceeding 0.5 million Btu per hour, and combustion gases are vented to the ambient air (40CFR, Section 279.23).

2.2 Recycling options for used oil

Used oil can be recycled to produce re-refined lubricating oil, fuel oil or a distillate fuel known as marine diesel oil (MDO). Re-refining used oil to lubricating oil and MDO produces asphalt as a by-product. Used oil can also be used as refinery feedstock to produce a variety of petroleum products. (See diagram on page ix.)

2.2.1 Re-refining to lubricating oil

Used oil is re-refined to yield base oils that are blended into lubricating products, thus reducing the consumption of virgin oils (Technical Working Group of the Basel Convention, 1997). Re-refining restores the physical and chemical properties of lubricating oil so that it can go back to its original and intended use (CIWMB, 2003b). Used oil contains 70 to 75 percent lubricant base oil and less energy is required to produce the same amount of base stock from used oil than from crude oil (Kajdas, 2000a, 2000b).

Re-refining technologies two decades ago used low-yield acid/clay processes that generated large quantities of acid muds with high levels of sulfur, metals and metalloids that posed waste disposal problems (Gourgouillon et al., 2000). Today’s processes can

produce high-quality base oils comparable to lubricants derived from crude oil. Current re-refining technologies generally involve vacuum distillation of the dehydrated waste oil, followed by hydrotreatment of the distilled stocks (Kajdas, 2000b).

Vacuum distillation recovers lubricating oil hydrocarbons, while removing light-end fuels from the base oil (Frazier, 1998). The light-end fuels can be burned onsite for energy (Graziano et al., 1995), or sold to industrial furnaces and boilers (CIWMB, 2003a). Most of the contaminants are concentrated in the vacuum distillate residue. The subsequent hydrotreatment step is a hydrogenation process that removes about 90 percent of contaminants such as nitrogen, sulfur, oxygen and metals from liquid petroleum fractions (OSHA, 1999). This step also reduces polynuclear aromatic components and higher-boiling halogenates and polar compounds. Other re-refining processes include chemical pretreatment, solvent extraction, wiped-film (or thin-film) evaporation, and clay polishing (Kajdas, 2000a).

2.2.2 Re-refining to marine diesel oil

Used oil can also be re-refined to produce marine diesel fuel (also known as “marine diesel oil” or MDO, and “marine distillate B” or DMB). The process employed to produce MDO involves distillation to remove light ends and water, and the final separation of the distillate from contaminants (bottoms) (Boughton, 2004). Another process involves dehydrating used oil in a flash tower, followed by two stages of vacuum distillation (Graziano et al., 1995).

2.2.3 Reprocessing and blending into fuel oil

Another waste management option for used oil is to recover the heating value by reprocessing it to a fuel oil (Technical Working Group of the Basel Convention, 1997). Used oil has a heating value of about 138,000 Btu/gal, which is nearly equivalent to that of crude oil (Graziano et al., 1995). The recycled oil is marketed for use in asphalt plants, industrial boilers, electric utilities, steel mills, cement/lime kilns, pulp and paper mills, and commercial boilers (American Petroleum Institute, 2004). The reprocessed oil is also used as fuel oil cutter stock, a blending component for residual fuel oil (Kajdas, 2000a).

Reprocessing involves the removal of water and sediment by settling, followed by filtration to remove particulates, and blending to control ash (i.e., solid contaminants and metals present in the fuel in soluble compounds; ash is the inorganic solid residue left after combustion) (Plaza Marine Fuels, 2003). Reprocessing typically does not remove heavy metals and halogens in the used oil (Graziano et al., 1995). Thus, unless combusted under controlled conditions (e.g., stacks with “scrubbers” designed to capture contaminant emissions), use of the reprocessed fuel is likely to release toxic constituents (Kajdas, 2000a). In large volume reprocessing operations, water, light-end fuels and chlorinated solvents are removed by distillation, centrifuges are used for more efficient particulate removal, and/or a chemical treatment step is included to break emulsions and reduce the content of ash and sulfur (Graziano et al., 1995).

2.2.4 Reprocessing and blending into other petroleum products

Although it can only supply a fraction of the feedstock required by refineries, used oil can be used to replace crude oil feedstock in the petroleum refining process. A pretreatment

step is necessary due to the high concentration of inorganics in used oils that can deactivate refining catalysts and foul equipment surfaces, as well as the presence of halogens that can lead to costly corrosion (Graziano et al., 1995). In California, crude oil refineries are not permitted to process hazardous wastes such as used oil.

The total amount of used oil collected in California in one year is insignificant compared to the amount of feedstock consumed by the State's refineries. California's oil refineries process approximately two million barrels (84,000,000 gallons) of feedstock each day (CEC, 2004). Hence, the 100 million gallons of used oil collected for recycling in 2002 would represent less than two days' worth of feedstock.

2.2.5 Effect of recycling processes on the properties of recycled products

Table 2 presents certain properties of new (virgin) motor oil, used oil, and the products of used oil recycling, namely: re-refined lubricant base oil, marine diesel oil, and fuel oil cutter (from two different recycling facilities). The information in the table illustrates how recycling processes – from the minimal treatment to remove water and solids to produce fuel oil, to the distillation processes that yield re-refined oil and marine diesel oil – alter the properties of used oil to generate a distinctly different product.

Table 2. Properties of New Motor Oil, Used Oil and Recycled Oil Products

Property	New motor oil[a,b,c] *(10W-40)*	Used motor oil[d,e, f]	Fuel oil cutter[g,h]	Re-refined lubricating oil[i] *(300 Neutral base oil)*	Re-refined marine diesel oil (DMB)[j,k]
Boiling point, ^{o}F	650-1000[a]		185-1,040		364[f]
Density at 15.6^{o}C	0.880[b]	0.885[d]	0.910	0.871[g]	0.880[h]
Appearance	Amber to dark amber		Dark amber to dark brown	Bright and clear[g]	Dark amber to brown
Viscosity cSt	88.0 at 40oCa; 13.5 at 100°Ca	71 at 37.7^{o}C[e]	42 at 50°C	54 at 40°C[g]; 7.4 at 100°C[g]	7.28 – 12 at 40°C[f,h]
Bottom solids and water, % vol		6.0[e]	2.0 (max)		0.25 max[h]
Sulfur, % mass	0.5[j]	0.29-0.5[d,f]	0.4-0.5	0.07[g]	0.3[h]
Flash point (F)	415[a](min)	210 (min)[e]	150 (min)	435 (min)[g]	150 (min)[h]
Ash % (m/m)	1.0[c]	0.65[f]	0.3-0.6	0.001[g]	0.002[l]
Zinc (ppm)	1,400[b]	90-1,550[f]	700-900		
Calcium (ppm)			700-1,000		
Phosphorus (ppm)			600-1,200		

a. Potter and Simmons, 1998
b. Pennzoil, 2002
c. Hackett, 2004
d. Environment Canada, 2004
e. U.S. EPA, 1984
f. U.S. EPA, 1993
g. Evergreen Oil, Inc. 2003b
h. DeMenno/Kerdoon, 2004a, DeMenno/Kerdoon, 2004c
i. Evergreen Oil, Inc., 2003a
j. DeMenno/Kerdoon, 2004b, DeMenno/Kerdoon, 2004d
k. Ennis, 2004

NOTE: Full tables presenting comparisons among different marine fuels and recycled oil products can be found in Appendix A.

Sulfur is greatly reduced in the re-refining process that yields lubricant neutral base oil. (The sulfur levels in the latter are, in fact, lower than those found in new motor oil; this is attributable to the presence of sulfur in the additive packages of commercial motor oil products.) Distillation of used oil also reduces ash levels by almost two orders of magnitude in the resultant re-refined base oil and marine diesel oil.

2.3 Management of California used oil

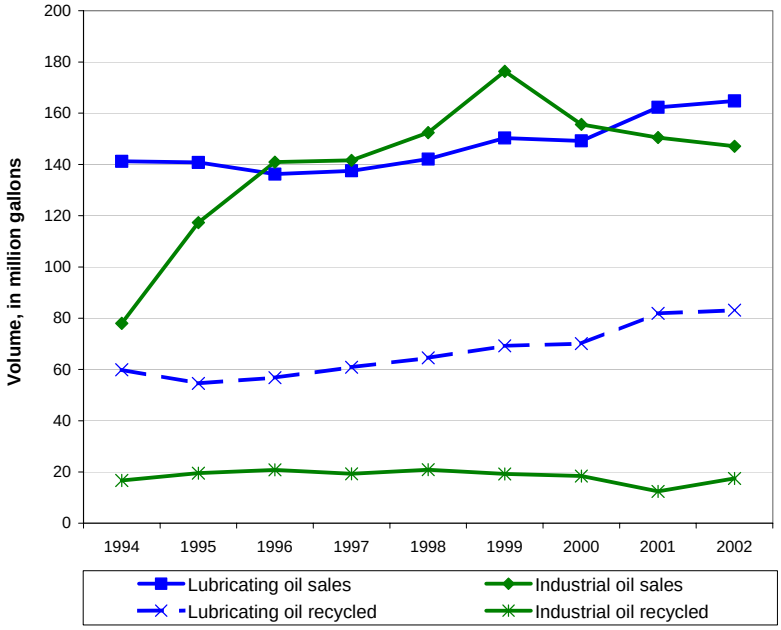
Used oil is consistently a significant portion of California's hazardous waste stream. Typically, used oil constitutes 29 to 36 percent of the "recurrent waste" shipped offsite annually. (Recurrent wastes are those that are routinely generated, and do not include hazardous wastes from operations such as contaminated site cleanups, or from removal of asbestos or PCB-contaminated equipment.) (DTSC, 2004)

2.3.1 Volumes of California used oil recycled

Operators of used oil recycling facilities must submit quarterly reports to CIWMB providing estimates of the number of gallons of used lubricating oil and used industrial oil received at the facility. CIWMB regulations also impose record-keeping requirements on these facilities (Sections 18641-42, Title 14, California Code of Regulations).

The volume of used oil recycled has generally shown upward trends over the years. Figure 2 shows the volume of oils sold and recycled in California, based on data reported to CIWMB by oil manufacturers and sellers, and recycling facilities, and presented by CIWMB in its *2002 Used Oil Recycling Rate Annual Report* (CIWMB, 2004a). Although the annual volumes of lubricating and industrial oils sold since 1996 have been comparable – ranging from about 140 million to 160 million gallons -- the volume of recycled lubricating oil has been about three to four times higher than industrial oil during the same period of time.

Figure 2. Volume of Oils Sold and Recycled in California

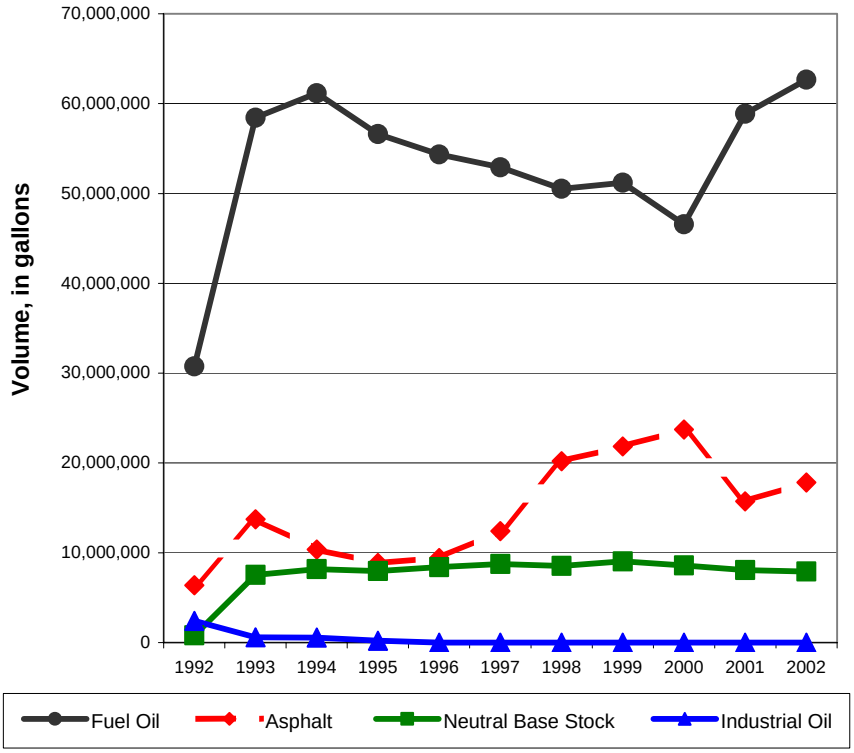


Source: California Integrated Waste Management Board

2.3.2 Products of used oil recycling

Recyclers must also report to CIWMB the volumes of fuel oil, industrial oil, neutral base stock and asphalt they produce from used oil (Section 18641, Title 14, California Code of Regulations). For purposes of reporting to CIWMB, the term "fuel oil" includes recycled oil to be combusted as fuel, fuel oil cutter (sometimes referred to as recycled oil cutter), and marine diesel oil. Asphalt flux, a by-product of the distillation processes that yield lubricant base stock or MDO, is a dark brown-to-black tar-like material that is used as a roofing tar, and as a binder for use in asphalt concrete. The heavy metals and other contaminants in used oil are concentrated in the asphalt; however leaching tests conducted by the Department of Toxic Substances Control have shown that the heavy metals are bound within the tar matrix and insignificant leaching occurs (Boughton and Horvath, 2004). Figure 3 shows the volumes of recycled oil products derived from used oil, as reported by recycling facilities to CIWMB (CIWMB, 2004b).

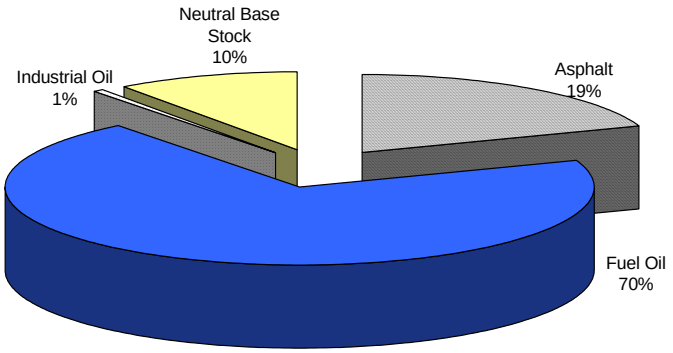
Figure 3. Recycled Oil Products from California Used Oil



Source: California Integrated Waste Management Board

Only one California recycler (Evergreen Oil) produces lubricant base stock. Blenders combine the base stock with an additive package to meet specified performance requirements, and generally sell the re-refined lubricating oil in bulk to distributors. The number of re-refining facilities producing lubricating oil in the United States has decreased significantly, from about 13 in 1983 (U.S. EPA, 1984) to only two today, including the one in California (CIWMB, 2003). Re-refining in California produces only 2.5 percent of the State's base lubricating oil production capacity and 0.3 percent of the U.S. capacity (Boughton and Horvath, 2004).

Figure 4. Recycled Oil Products from California Used Oil
(Average percentage of total, 1992-2002)

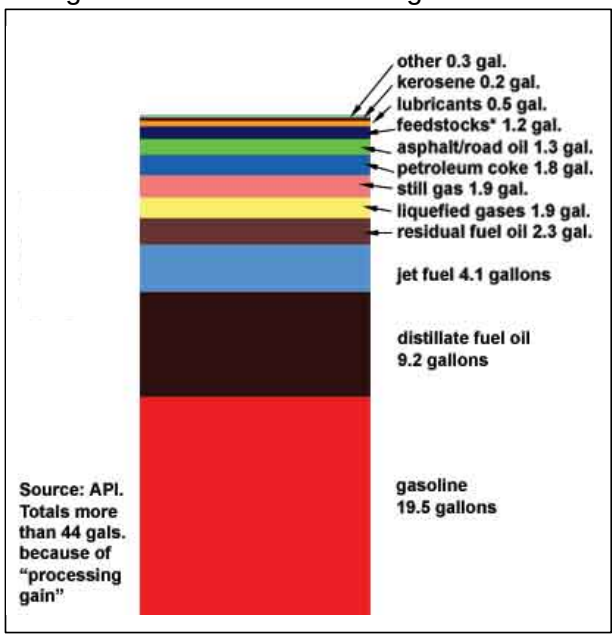


Source: California Integrated Waste Management Board

Quarterly reports submitted by recycling facilities to CIWMB indicate that fuel oil comprises the highest volume end-product of used oil recycling (CIWMB, 2004b) (see Figures 3 and 4). In 2002, California recyclers produced approximately 50 million gallons of fuel oil from used oil. Only 3 million gallons/year of used oil fuels (i.e., fuel oil cutter) are consumed in the State because of strict air pollution requirements and the relatively poor quality fuel made from the used oil (i.e., generally high sulfur and ash content). The majority of used oil that is processed into fuel oil cutter stock is shipped out of State and overseas for use as fuel. (Boughton and Horvath, 2004).

3.0 FUELS USED IN MARINE VESSELS

Figure 5. Petroleum Refining Products



The refining of crude oil yields a number of major products, including gasoline, distillate fuels, kerosene, liquefied petroleum gas, lubricants, and residual fuels. Figure 5 shows the typical products resulting from refining a barrel (42 gallons) of crude oil (California Energy Commission (original source: American Petroleum Institute), 2002). Marine engines use distillates, residual fuels, or a blend of both (U.S. EPA, 2003b). These blends are also referred to as intermediate fuels.

"*Bunker fuel*" is a general term often used to refer to fuel burned in ships for propulsion, and largely consists of residual fuel. Bunker fuel is also burned for energy in power plants, cement kilns and other industrial facilities.

3.1 Overview of marine fuels

Specifications for marine fuels officially carry the first letters “D” for distillates, or “R” for residual fuels, followed by the letter “M” signifying their use as “marine” fuels (U.S. EPA, 1999). Distillates are composed of petroleum fractions of crude oil that are separated in a refinery by a distillation. There are four specifications (developed by the American Society for Testing and Materials, or ASTM) for marine distillate fuels (U.S. EPA, 2004b):

> DMX, a special light distillate with a lower flash point intended mainly for use in emergency engines.
>
> DMA (also called marine gas oil, or MGO), a general purpose marine distillate commonly used for tugboats, fishing boats, crew boats, drilling rigs and ferry boats that contains no traces of residual fuel.
>
> DMB (also called marine diesel oil or MDO), used for larger marine vessels (Category 2 and 3 engines), including oceangoing ships (often as a blending agent), and is allowed to contain a trace of less refined fuel as a result of flowing through pipes used for residual fuel.
>
> DMC, a grade of marine fuel that may contain some residual fuel and is often a residual fuel blend.

A large portion of marine distillate fuels is land-based distillates rebranded for marine use. For example, No. 2 on- and off-highway fuels are rebranded and supplied as DMA. (In the north and northeastern states, No. 2 fuel oil for home heating may be rebranded as DMA.) A study of marine fuel use patterns conducted in 1999 for U.S. EPA estimated that as much as 90 percent of the DMA and DMB was manufactured originally as a land-based fuel, primarily as No. 2D high sulfur (for off-highway use), and rebranded for marine use (U.S. EPA, 1999).

Residual fuel oils are the heavier oils that remain after the lighter fractions have been distilled away in the refining process. Residual fuel is inexpensive compared to other crude oil-derived products, and contains high levels of sulfur and nitrogen (U. S. EPA, 2003a). Polycyclic aromatic hydrocarbons (PAHs) and metals become concentrated in residual fuel. Residual fuel oils may be directly produced from the distillation process, as well as from a complex process of selection and blending of various petroleum fractions to meet definite specifications (Weisman, 1998).

Residual fuel oils include grades Numbers 5 and 6 fuel oils and also Bunker C (Energy Information Administration, U.S. Department of Energy, 2003). In addition to their use as fuel, residual fuel oils are used as feedstock to produce lighter, more valuable fuel fractions. Residual fuels contain high molecular weight hydrocarbons, have a very high viscosity at ambient temperatures, and must be heated prior to combustion in ship engines. (Viscosity is the resistance of a fluid to flow, and is measured in centistokes (cSt) and quoted at a reference temperature of 50°C for residual fuels.) There are 15 residual fuel grades in national and international specifications, with individual grades designated using the letters A through H, K and L, and a number signifying the

viscosity limit. Hence, RMA-10 is “Residual Marine Fuel A” having a maximum viscosity of 10 centistokes at 100°C (U.S. EPA, 1999).

The International Standard Organization (ISO), in cooperation with the marine and petroleum industry, has set forth specifications for marine fuels supplied worldwide for use onboard ships. The following four fuel grades are most frequently supplied for use by ships (Vis, 2003a; U.S. EPA, 1999):

> IFO180 (Intermediate Fuel Oil 180, also known as RME25 and RMF25), a blend of distillate and about 88 percent residual fuel, with a viscosity of 180 centistokes at 50°C;
>
> IFO380 (also known as RMG35 and RMH35), a blend of distillate and about 98 percent residual fuel, with a viscosity of 380 centistokes at 50°C;
>
> MDO (marine diesel oil, also known as marine distillate fuel B or DMB), sometimes a blend of marine gas oil and heavy oil; and
>
> MGO (marine gas oil, also known as marine distillate fuel A or DMA), 100 percent distillate, used in small and medium-sized compression-ignition engines, such as tugboats, fishing boats, crew boats, drilling rigs and ferryboats.

The distillate recycled fuel oil product MDO is comparable to crude oil-derived distillates used as marine fuels. Its low ash content (0.002 percent weight or 20 ppm), low sulfur and viscosity content makes it particularly desirable for blending in fuels for harbor craft or for oceangoing vessels. Most harbor craft, however, use the readily available and competitively priced on-road and off-road diesel fuels meeting U.S. EPA and California Air Resources Board (CARB) standards.

Fuel costs make up about 40 percent of the overall operating costs in ships (Legislative Analyst's Office, 2001). Because distillates are more expensive than residual fuels, the greater the proportion of distillate fuel in an intermediate fuel, the higher the price. Table 3 compares the prices of the four fuel grades at different major shipping ports (Bunkerworld, 2004b).

Table 3. Marine Fuel Prices in US Dollars per Metric Tonne (as of May 13, 2004)

Port	IFO 380	IFO 180	MDO	MGO
Los Angeles	$179.00	$198.00	$415.00	---
New York	$192.00	$203.00	$339.00	---
Houston	$180.50	$187.00	$294.50	---
Singapore	$186.00	$192.00	$319.00	$328.00
Rotterdam	$170.00	$180.50	$295.50	$328.50
Fujairah	$184.50	$191.50	$330.00	$330.50

The fuel capacity of oceangoing vessels varies substantially, with relatively newer ships having fuel capacities in the order of 15,000 to 20,000 metric tonnes (Legislative Analyst's Office, 2001). A bunkering stop might result in the purchase of between

3,000 to 4,000 metric tonnes. Hence, a purchase of IFO 380 could cost as much as $768,000.

3.2 Types of marine engines

Traditionally, marine engines have been either steam- or diesel-powered, although virtually all engines built since 1980 have been the latter. There are three types of marine diesel engines (U.S. EPA, 2003b):

> *Category 1* engines are similar to land-based non-road engines used in construction and farm equipment, and have a rated power greater than or equal to 37 kilowatts and a per-cylinder displacement less than 5 liters.
>
> *Category 2* engines are most often similar to locomotive engines, and have a per-cylinder displacement at or above 5 liters but less than 30 liters.
>
> *Category 3* engines are very large engines used for propulsion on large oceangoing vessels such as container ships, tankers, bulk carriers, and cruise ships; they have a per-cylinder displacement at or above 30 liters. There are no land-based mobile source counterparts for these engines, although they are similar to engines used to generate electricity in certain power plant operations.

Category 1 and Category 2 marine diesel engines are used as propulsion engines (i.e., an engine that moves a vessel through the water or directs the movement of a vessel) on tugboats, fishing vessels, supply vessels, and smaller cargo vessels. They are also used as auxiliary engines to provide electricity for navigation equipment and crew service or other services such as pumping, powering winches, or handling anchors. Category 3 engines generally operate on the less expensive, high-sulfur residual fuel for their main propulsion engines to cruise the ocean.

3.3 Bunker fuel: A historical perspective

Historically, bunker fuel was considered to be a waste produced from the refining of crude oil. It was to the refiners' benefit to give this residue away to the shipping industry. However, when oil prices soared during the first oil crisis in the early 1970's, this black viscous material became a valuable commodity. Starting in the 1980's, the price of bunker fuel, as with other petroleum products, increased and became volatile.

Increased world trade has been accompanied by the growth of the international shipping fleet. Although the size, cargo capacity and number of ships has increased, the demand for bunker fuel has not increased proportionally because of greater fuel efficiency. The amount and quality of residual oil per barrel of crude oil refined has declined at the same time because of technological advances that increased the yield of higher value distillate products. The engines of newer ships are more sophisticated, have tighter tolerances and thus greater susceptibility to damage from certain fuel constituents (Hill, 2003).

Proposed new regulatory standards designed to curb air pollution call for cleaner distillate fuels for marine vessels, especially when operating in populated coastal waters. Administration of the new requirements is complex because maritime vessels travel globally visiting ports with different regulations and fueling capabilities. The

industry is multinational; the vessels can have many owners and fuel suppliers. Increasingly, to meet regulatory requirements for the ports on its itinerary, a ship must maintain separate fuel tanks at increased costs.

3.4 Bunker fuel and used oil

Because of its low density and combustion value, used oil has been added to bunker fuels in some parts of the world, including California, for over 25 years (CIMAC Heavy Fuel Oil (HFO) Working Group, 2003). Unprocessed (raw) used oil was a lower cost fuel blend stock for bunker suppliers and shippers concerned with tight profit margins. In the past, many ships would dispose of their own used auxiliary engine crankcase oil by placing it in their fuel tanks. A few countries (e.g., Australia, New Zealand, U.S.) reportedly encouraged the blending of small amounts of used oil with bunker fuel as an environmentally preferred means of disposal (Kassinger, 2004a). The practice did not appear to be as prevalent in Europe as in North America.

In the 1990s, 10 to 25 percent of all marine fuel sold on the United States West Coast was estimated to have been blended with used oil, compared to about 2 to 4 percent of the fuels in the rest of the world. Historically, bunker fuel analyses showed used oil at concentrations ranging from 1 to 3 percent -- a very small percentage of the total fuel volume.

3.4.1 Shipping industry concerns

During the mid-1990s, the shipping industry became increasingly concerned over the addition of “chemical waste” to bunker fuels, and the adverse consequences of this practice on ship engines (Bunkerworld, 2003). Much of the concern in the United States appeared to be the result of a 1991 incident involving the *Kalamos*, a ship unknowingly supplied with fuel mixed with raw used oil (Lloyd's List, 2002). The bunker fuel supplier, a large West Coast independent, was sued for damages allegedly caused by the presence of used oil in the fuel. Although the independent supplier prevailed in the lawsuit, the practice of blending used oil into bunker fuel has since been highly contentious. Other episodes of bunker fuel contamination not related to used oil include: severe filter plugging in 15 ships due to polypropylene particles in fuel (1997); the “sour acid diesel affair,” which involved 17 ships that received bunker fuel containing “acid-damaged“ palm oil (1999); and an incident where 10 ships received organic chemicals instead of bunker fuel from bunkering barges in Singapore Harbor (2001) (Aabo, 2003; Bunkerworld, 2000).

Although used oil was not always involved in fuel contamination incidents, most shippers, nevertheless, became unwilling to accept used oil in bunker fuel because it could provide a route for waste materials to enter the bunker fuel pool. Used oil can easily conceal any unwanted or waste chemicals added to it because of its dark color. Hazardous wastes and other chemicals – including solvents, metals, PCBs and acidic materials – have been mixed with used oil for a number of reasons, not all ill-intentioned. These include: lack of knowledge of the regulations, lack of understanding of the consequences, ignorance that mixing had occurred prior to taking control of the fuel, and accidents or mishandling. Some in the industry maintain that used oil or hazardous waste generators, collectors or transporters may be motivated by profit gained from avoiding hazardous waste disposal fees as well as from selling

waste as product (Vis, 2003b). It is difficult to establish any factual basis for these claims, particularly in the United States.

Incidents of engine damage due to waste chemical contamination of fuel are rare, but can have severe consequences. The loss of engine power in a vessel is a very dangerous situation, as the ship cannot be controlled or maneuvered. Repairing damage to the very large four-stroke engines of oceangoing vessels often involves great expense.

In addition to increasing the risk of waste chemical contamination, used oil itself has also been implicated as a likely cause of engine damage. Those opposed to the blending of used oil in fuel cite laboratory studies demonstrating its possible adverse effects on vessel engine centrifuge performance, as well as accelerated turbocharger fouling (due to used oil metal levels contributing to ash loading), accelerated wear rates of the engine components, deposits forming and fouling the combustion zone, or fuel pump damage (due to increased abrasives and/or cavitation damage due to water) (CIMAC HFO Working Group, 2003).

Many fuel buyers include a clause stipulating that the fuel supplied to them must contain no used oil so as to avoid liabilities for damaging engines and violating fuel regulations that do not allow blending with untreated used oil (CIMAC, 2003).

3.4.2 Fuel testing to ensure quality

It is essential that a ship's fuel meet specifications and be free of contaminants for the proper operation and maintenance of its engine and exhaust systems. To ensure fuel quality, it is standard practice for ship operators to take fuel samples in-line during delivery, and send these to a third-party laboratory for analysis. The fuel is held in the ship's tank until analytical results are received. When testing shows that the fuel does not meet specifications, the vessel's fuel tank has to be pumped out at great cost. The greater problem is that some of the chemicals which damage ship engines are "unknowns" or impossible to anticipate and thus are not included on the list of standard fuel analyses. A fuel can be submitted to fuel specification tests and be found compliant with the standard, but still prove to cause fuel delivery problems and engine damage. The occurrence of such "rogue" fuels is unpredictable, and establishing the identity of the chemicals responsible for the damage (often referred to as "phantom" damages) is often difficult (Vis, 2003b).

In addition to determining whether the fuel meets industry specifications, analyses in recent years have also been carried out to determine the levels of zinc, calcium and phosphorus. Because these chemicals are commonly used in lubricating oil additives, the presence of all three above certain levels serves as an indicator of the presence of used oil. In the past two to three years, samples of marine fuels sold in the United States that were tested at two commercial fuel testing laboratories have rarely shown evidence of used oil (Kassinger, 2004a; Eley, 2004).

4.0 USED OIL AND BUNKER FUEL: HUMAN HEALTH IMPLICATIONS

There are currently no standards for ship air emissions at California's ports. Existing national, State and local measures to curb air pollution at California's coastline have achieved only modest emission reductions. Increasing air quality concerns and the need for further reductions in air pollution from oceangoing ships has prompted California to propose an ambitious, multi-pronged approach to addressing these emissions (see section 5.1.3). It should be noted that the proposed emission reduction strategies primarily address oxides of sulfur and nitrogen, particulate matter, ambient ozone and other greenhouse gases; other toxic emissions (e.g., metals, polycyclic aromatic hydrocarbons) that are also of potential human health concern are not currently addressed (Cal/EPA, 2003).

Marine vessels are a significant source of emissions in California air basins where ports are located, such as the South Coast, the San Francisco Bay Area, and the San Diego Air Basins. In the South Coast Air Basin, for example, ships and commercial boats were estimated to contribute about 51 percent of the oxides of sulfur, about 5 percent of the oxides of nitrogen, and up to 3 percent of the particulate matter emissions in 2003 (South Coast Air Quality Management District, 2003). Since major port facilities are located near the State's three largest urban areas, marine vessel emissions have the potential to impact the health of a significant portion of the State's population.

This project was based on the premise that used oil or used oil-derived fuels are added to bunker fuel combusted in marine vessels. (As previously discussed, bunker fuel is a blend consisting of up to 95 percent residual fuel and up to 15 percent distillate.) Hence, the assessment was intended to address the following question:

Does adding used oil to bunker fuel change the human health risks associated with air emissions from marine vessels?

As previously discussed, adding used oil (or fuel oil derived from used oil) to bunker fuel has been on the decline and probably occurs infrequently today. Although the practice appears to have been common up until about five years ago, OEHHA found no studies in the literature concerning the addition of used oil to marine fuels and possible impacts on human health. Following a search for chemical constituent and emissions data in the published literature, OEHHA determined that data are lacking to adequately identify and quantify the levels of hazardous chemicals in emissions from the combustion in ships of used oil and bunker fuel. Without this information, the subsequent steps of a risk assessment cannot be carried out – i.e., estimating levels of exposure in order to derive risk (for carcinogens) or hazard estimates (for non-carcinogens).

Although any incremental health risks that might result from the addition of used oil to bunker fuel cannot be quantified at this time, the sections that follow discuss data that would be relevant in conducting such an assessment, should more complete data become available.

4.1 The risk assessment process for estimating health risks from fuel combustion

Figure 6 illustrates the health risk assessment process that would be carried out for combustion of fuels in marine vessels. In order to estimate exposures and risk, the following steps are required:

- Characterization of the chemical composition of the fuels (source characterization);
- Determination of emission rates of each potentially hazardous chemical from marine vessels (emissions characterization);
- Estimation of the downwind concentration of each potentially hazardous chemical (air dispersion modeling); and
- Estimation of chemical- and pathway-specific risks and hazards resulting from exposure to these emissions (exposure assessment and risk characterization).

4.1.1 Source characterization

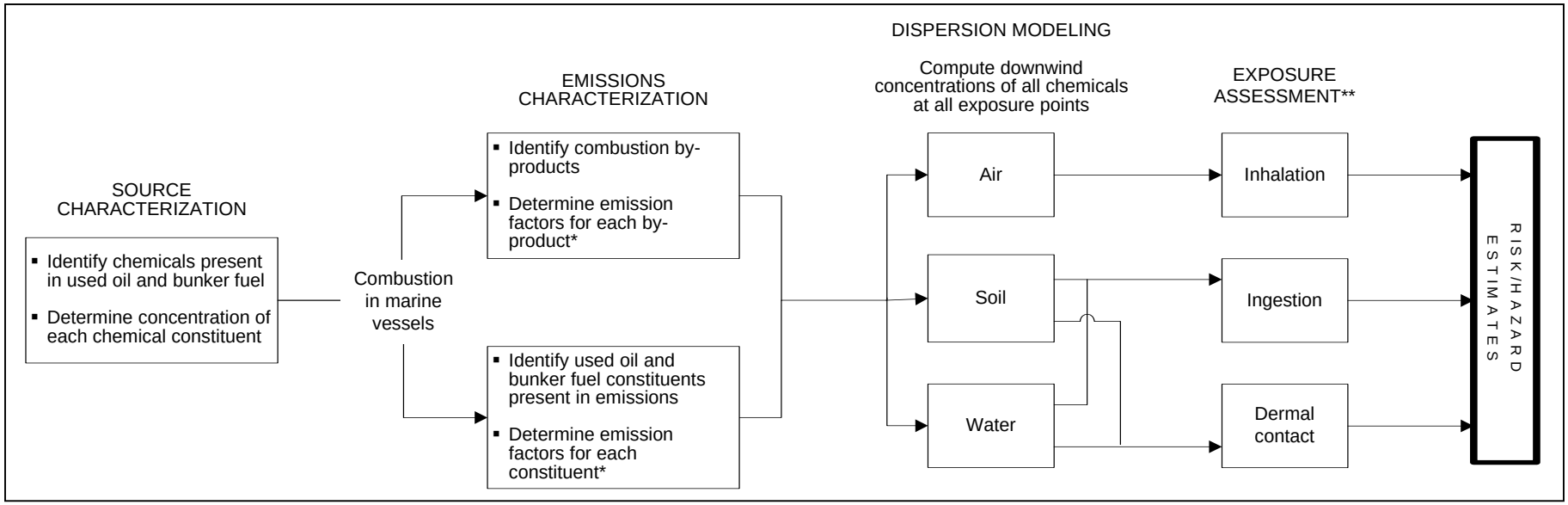
As an initial step, the source – i.e., the fuel -- must be characterized in terms of its hazardous constituents and the concentrations at which they occur. In the absence of constituent-specific analytical data for used oil-derived fuel oil, OEHHA relied upon analytical data on used oil; since only physical treatment is involved in recycling used oil to fuel oil, the chemical composition of both materials can be reasonably expected to be similar. The hazardous constituents identified in both the used oil and marine fuels (i.e., distillate and residual fuel) and their respective emissions would be evaluated in parallel using current risk assessment methodologies to compare the estimated risks. Additionally, the risks associated with burning a blend of used oil and bunker fuel – in any ratio – could be estimated from this information using standard risk assessment methodologies.

4.1.2 Emissions characterization and air dispersion modeling

Because the burning of fuels results in the release of airborne contaminants, the hazardous constituents in emissions must be identified and quantified. Two general classes of chemical emissions result from combustion. The first consists of compounds that are present in the fuel and escape alteration by the combustion process. The mass of metals, for example, is not altered by combustion and therefore is assumed to be present in the exhaust emissions in direct relation to the amount present in the fuel. A small fraction of the organic compounds present in fuel may also be released as emissions because the efficiency of all combustion devices is less than 100 percent.

The second class of emissions consists of chemicals that are not present in the fuel, but are created by the combustion process. These chemicals, which are generically referred to as products of incomplete combustion, arise because the temperatures and pressures of internal combustion engines are sufficient to chemically alter the constituents in fuel, but are not sufficient to destroy them completely.

Figure 6. The Process of Estimating the Human Health Impacts of the Combustion of Used Oil as Bunker Fuel



* Emission factors = mass of constituent or by-product per mass of fuel burned

** Not shown are the indirect exposure pathways, i.e., those that result from ingestion of plants (fruits and vegetables) and animal products (meat, milk and milk products, and eggs). For certain classes of persistent contaminants such as PAHs and chlorinated dibenzodioxins and dibenzofurans, these indirect pathways may be the primary routes of exposure

Airborne concentrations of individual constituents in engine exhaust can be estimated by using *emission factors* and *air dispersion modeling*. An emission factor is expressed as a mass of contaminant output per amount of fuel burned (e.g., kilograms SO_x per tonne fuel), or it can be based on energy output (e.g., grams SO_x per kilo-watt hour). These constituent-specific factors are dependent on the combustion device, the engine's power output and the fuel. Emission factors are combined with the results of air dispersion models to estimate downwind concentrations for individual contaminants in air and, following deposition, in water and soil. Individuals or populations may be exposed to contaminants via inhalation of airborne contaminants, ingestion of contaminants in soil, water, or foods (such as homegrown vegetables), and dermal contact with contaminated soil or water.

4.1.3. Exposure assessment and risk characterization

In conducting an exposure assessment (see Figure 6), exposure point concentrations for each hazardous constituent are calculated for each affected environmental media (air, soil, water), and exposure estimates determined for all relevant routes of uptake (inhalation, ingestion, dermal contact). Exposure point concentrations are derived either from direct sampling of environmental media or by using modeled data, such as airborne concentrations estimated using an air dispersion model. The exposure point concentrations and toxicity criteria (cancer potency factors and reference concentrations) for individual chemicals can then be used to estimate cancer and other noncancer health risks from exposure to pollutants in marine emissions.

4.2 Characterization of hazardous constituents in used oil and bunker fuel

OEHHA searched the literature for available data on hazardous constituents in used oil and in bunker fuel. The sources reviewed included peer-reviewed scientific journals, technical reports in the open scientific literature, governmental reports, and industry web sites. Much of the analytical data on used oil were collected in the mid-1980s to mid-1990s, evidently for purposes of informing regulators about appropriate standards for the management of used oil. The data are generally limited to a few select contaminants that are regulated in recycled oil combusted for energy recovery: arsenic, cadmium, chromium and lead. Regulatory limits are specified for halogens and PCBs as well. Further, changes in the past decade in lubricating oil products, automobile engines, and fuel formulations (such as phasing out of tetraethyl lead as a gasoline additive beginning in 1973) raise questions about the relevance of data from a decade ago in conducting a health risk assessment from burning today's used oil. Information on the presence of other potentially hazardous constituents that occur in used oil – such as other metals, polycyclic aromatic hydrocarbons (PAHs) and volatile organics -- is limited.

Similarly, constituent data were also limited for bunker fuel. Since crude oil and its products are highly complex and variable mixtures, constituent-specific chemical analysis is a difficult task. Moreover, the data required to conduct a risk assessment are often different from those required by the petroleum industry, whose objective is to determine the performance characteristics of petroleum mixtures (Weisman, 1998). Complete assessment of these complex mixtures is also hampered by costs and by analytical limitations (Massachusetts Department of Environmental Protection, 1994).

Used industrial oils make up about a quarter of the used oil received at recycling facilities (see Figure 2). Due to the diversity of operations at industrial facilities, the composition of used industrial oils collected for recycling is expected to be highly variable (U.S. EPA, 1984). A review of the literature found a paucity of constituent data for these oils. Hence, the data presented in this section predominantly reflect constituent concentrations in used automobile *crankcase* oil.

With the exception of one dataset (Grimmer et al., 1981), the data presented in this report are primarily from studies within the past 20 years. These studies were selected because they are more likely than older studies to have derived constituent data using more sensitive analytical methods, and they are from samples that better represent the composition of today's crankcase oils. The studies are listed and described in the boxed text on page 20. A complete compilation of the analytical data found by OEHHA is presented in Appendix B.

4.2.1 Composition of new lubricating oil

Crankcase oil consists primarily of a base lubricating oil that has a variable chemical composition depending on the source of crude oil and the design of the refinery where the base oil was produced. Lubricating base oil is a heavy end distillate of crude oil with a boiling range of 325-600°C. It contains approximately 44 percent straight chain and branched alkanes (primarily C18 through C34), 29 percent cycloalkanes, 22 percent aromatics, 4.2 percent total alkyl aromatics and 3.2 percent total naphthalenes (Potter and Simmons, 1998). However, Pruell and Quinn (1988) reported that the concentrations of naphthalene, alkyl naphthalenes, biphenyl and 3-, 4-, and 5-ring PAHs were all non-detect in new lube oil (limit of detection was 5 ppm), suggesting that PAHs accumulate in oil from gasoline and incomplete combustion of gasoline.

Various additives are introduced into crankcase oil to improve lubricating qualities and prolong its effective lifespan. Additives usually comprise 10 to 20 percent of the volume of finished lubricating oil (U.S. EPA, 1984). Major additive classes include corrosion and rust inhibitors; antioxidants; emulsifiers, detergents and dispersants; viscosity and color stabilizers; and anti-wear additives. Additives may contain calcium, zinc, magnesium, molybdenum, barium, phosphorus, sulfur and bromine compounds.

The presence of chlorine in lubricating oil is of concern because of the potential for the formation of hydrochloric acid and chlorinated dibenzodioxins (and related chlorinated compounds) that might be generated during combustion. While chlorine-containing compounds are not deliberately added to today's engine lubricants, small amounts may be present (Hewstone, 1994). Chlorine can occur as a contaminant from chemical processing (i.e., from the use of a chlorinated intermediate in the manufacturing process, or from the use of aluminum chloride as a polymerization catalyst for oil additives), or as an impurity in raw materials such as magnesium and zinc oxides.

Sources of the analytical data presented

Meinz et al., 2004. This recent study of used oil composition was described in a draft report from Washington State's Department of Ecology. Nine samples were collected from the crankcases of eight gasoline engines, one sample from the crankcase of a diesel engine, one from the collection tank of a commercial oil change business. One sample of virgin lubricating oil was also analyzed. Samples were analyzed for the four regulated metals (arsenic, cadmium, chromium and lead), benzene and substituted monoaromatic compounds, halogenated solvents, and naphthalene. Please note, these data are from a DRAFT report and could change when the final report is released.

Sivia et al., 1998. This study, conducted by DTSC under contract with CIWMB, evaluated different sample preparation methods for analysis of metals in used oil.

Potter and Simmons, 1998. This source reports data on the composition of distillate fuels (No. 2 fuel oil and diesel #2) and residual oil (No. 6 fuel oil). Constituent data were reported in a 1998 Total Petroleum Hydrocarbon Criteria Working Group document, *Composition of Petroleum Mixtures*.

Brinkman and Dickson, 1995. Ninety-six samples were collected from various used oil sources (vehicle crankcase oil, quick lube oil, used oil tankers/feedtank and industrial oil) and tested for metals, chlorinated solvents and PAHs.

Lloyd's Register Engineering Services, 1995. This study primarily focused on evaluating marine pollutant emissions from various fuel types, but also evaluated bunker fuels for metals.

V*ermont Agency of Natural Resources, 1994*. Samples collected from gasoline and diesel vehicle maintenance facilities and one sample of virgin lube oil were analyzed for metals, halogens and PCBs. This was the most comprehensive study in that it evaluated all three categories of contaminants and compared concentrations detected in used oil with those found in virgin lube oil.

Upshall et al., 1993. In this study, one sample of crankcase oil was analyzed for PAHs.

U.S. Environmental Protection Agency, 1993. This 1993 report, *Emission Factor Documentation for AP-42, Waste Oil Combustion*, reports concentrations of trace elements, chlorine and sulfur found in used crankcase oil, distillate and residual oil. The waste oil includes used oil from vehicles and from industrial sources (e.g., metal working oils). These data were apparently based on samples collected and analyzed in 1982-83.

Pruell and Quinn, 1988. This study examined the accumulation of PAHs in lubricating oil samples collected periodically from a single vehicle. Oil from the same vehicle was also collected and analyzed at three regular oil changes, occurring after the car had been driven 3900, 4800 and 5800 miles. Data from the latter portion of the study are summarized in Appendix B.

U.S. Environmental Protection Agency, 1984. This report summarizes information acquired by U.S. EPA from 1981-1984. Analytical results from over 1,000 samples of various types of used oils are presented.

Grimmer et al., 1981. This 1981 study specifically inventoried PAHs found in used crankcase oil from gasoline and diesel engines. Although this is an older study, it was the most comprehensive analysis available reporting PAHs in used oil.

4.2.2 Composition and toxicity of used lubricating oil

The chemical composition of used crankcase oil varies widely and depends on the original crude oil, the mechanical condition and type of engine the oil is lubricating, the length of time that the oil remains in the engine, and the type of fuel combusted in the engine (i.e., gasoline or diesel fuel). Sources of contamination include additive breakdown products; engine blow-by (i.e., material which leaks from the engine combustion chamber into the crankcase where the oil resides); burnt oil, dirt and dust; metal particles from engine wear; and incomplete combustion of gasoline (U.S. EPA, 1984). It is reported that diesel fuel engine oil contains lower concentrations of volatile hydrocarbons from blow-by than gasoline engine oils. Furthermore, the PAH composition in used oil from diesel engines is different (and considered to be less carcinogenic) than that of gasoline engine oil (Clancey, 1999).

Used oil has been found to contain arsenic, barium, cadmium, chromium, lead, manganese, nickel, and zinc. The presence of these metals is due to the breakdown of lubricating oil additives (e.g., barium and zinc), wear from engine parts (e.g., arsenic, cadmium, chromium, nickel), or piston blow-by (e.g., lead in gasoline). Numerous other metals are present in used oils such as aluminum, copper, iron, magnesium, silicon and tin; however, they are generally not given much attention due to their low concentrations and low toxicities (Agency for Toxic Substances and Disease Registry, 1997).

Although PAHs are present in new lubricating oil at very low concentrations, used motor oil can become “enriched” with PAHs during the operation of an automobile engine. PAHs apparently concentrate in lubricating oil via transfer from gasoline or diesel fuel and their combustion products (U.S. EPA, 1984). Indeed, a study that analyzed PAH concentrations in new crankcase oil and further sampled the oil over the course of 6,000 vehicle miles found PAH concentrations to increase with engine usage (Pruell and Quinn, 1988). Most notable were the naphthalene levels, which increased by two orders of magnitude. Simple 2- and 3-ring aromatics were detected after the car had been driven just 212 miles, and 4-ring PAHS were detected after 728 miles. Complex 5-ring PAHs were detected in a sample that was collected at 5,800 miles. The authors concluded that used crankcase oil that is improperly disposed of might be a major source of PAH compounds released to the environment.

Used oil is listed under Proposition 65 (Safe Drinking Water and Toxic Enforcement Act of 1986) as a chemical known to the State of California to cause cancer (Title 22, California Code of Regulations, Section 12000). Animal studies have shown an increased incidence of skin tumors in mice after long-term skin exposures to used mineral-based crankcase oil from gasoline-powered cars, with more tumors observed in mice exposed to oil from cars driven the longest distances. The increase in carcinogenicity was attributed to accumulation of PAHs in the oils, given the correlation between tumor incidence and the PAH content of the oil (Agency for Toxic Substances and Disease Registry, 1997). In support of this hypothesis, McKee and Plutnick (1989) reported no tumors in mice exposed to new motor oil.

4.2.3 Constituents and toxicity of bunker fuel

Much of the available analytical data on marine fuels tends to focus on chemical constituents that can affect fuel performance or cause engine damage (e.g., metals such

as aluminum and vanadium). Limits on these constituents are generally included in fuel specifications, which must be adhered to by the blenders of marine fuels. Chemical constituent data presented here for purposes of comparison with used oil are for either residual or distillate fuels, since no constituent data specifically for bunker fuel (residual/distillate blends) were found.

Residual (heavy) fuel oil is listed under Proposition 65 (Safe Drinking Water and Toxic Enforcement Act of 1986) as a chemical known to the State of California to cause cancer (Title 22, California Code of Regulations, Section 12000). In a laboratory cancer bioassay, residual oil produced a benign skin tumor when tested by skin application to a group of 40 mice (Bingham et al., 1980.) Chemical constituents of residual fuel oil that are potentially tumorigenic include PAHs and arsenic.

Vanadium and nickel are two metals of potential health concern that have been also detected in used oil and bunker fuel. Inhalation of vanadium pentoxide has been shown to produce lung cancer in mice, and a number of nickel compounds are listed under Proposition 65 (Safe Drinking Water and Toxic Enforcement Act) as chemicals known to the State of California to cause cancer (Title 22, California Code of Regulations, Section 12000).

Tables 4 to 6 summarize analytical data that have been located for new lubricating oil, used lubricating oil, and distillate and/or residual fuel (bunker fuel). In the absence of data specific to marine distillate fuels, data for No. 2 fuel oil and No. 2 diesel are presented; these fuels are often rebranded for use as marine distillate fuels (see Section 3.1). The tables present data on the following:

- *Regulated chemicals*, i.e., constituents for which limits are specified in regulation (arsenic, cadmium, chromium, lead, halogens and PCBs);
- *Polycyclic aromatic hydrocarbons*; and,
- *Volatile organic chemicals*

Table 4. Concentrations of Regulated Chemicals in New Lubricating Oil, Used Oil, Distillate Fuel, and Residual Fuel (in ppm)
(Note: The single value shown is the mean of the data set; the range is shown in parenthesis. *ND* – Not detected; *NA* – Not available; *NR* - concentrations not reported due to "analytical difficulties")

	CA limits	New Lube Oil		Used Oil					Distillate Fuel*	Residual Fuel*	
		Meinz *et al.* 2004	Vermont 1996	Brinkman & Dickson 1995	Vermont 1996		Sivia *et al.* 1998	Meinz *et al.* 2004	USEPA 1993	USEPA 1993	Lloyd's Register 1995
					Gasoline Engine	Diesel Engine					
As	5	ND	NR		NR	NR	<2.5	0.12 (ND – 0.45)	0.8 (0.10-0.2)	0.8 (0.02-2.0)	(0.27 – 1.0)
Cd	2	ND	<0.25	ND (ND – 5)	<1.5 (ND –3.3)	2.4 (0.8 – 6.6)	1.03	0.17 (ND – 0.86)	0.3 (0.1-0.9)	2.3** (0.01-0.9)	ND
Cr	10	1.4	<2.0	10 (ND – 233)	3.2 (ND – 4.2)	3.9 (2.4 – 6.9)	<5	4.5 (2.0 – 17.6)	1.3 (0.5-2.8)	1.3 (0.1-1.7)	(ND – 0.39)
Pb	50	0.15	<20	29 (ND – 265)	47.2 (ND – 104)	57 (23.6 – 146)	42.5	13.2 (0.2 – 66.1)	1.8 (0.5-4.4)	3.5 (0.1 – 8.0)	(ND – 0.15)
Halogens	3000		<300		< 350	< 234					
PCBs	2		<5		< 5	< 5					
Sample size		1	2	96	17	4	1	9			6

* Chemical constituent data presented here are for either residual or distillate fuels, since no constituent data specifically for bunker fuel (residual/distillate blends) were found.
** The mean value reported in the reference is likely to be in error, as it does not fall within the range of values reported.

Table 5. Concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) in Used Oil, Distillate Fuel and Residual Fuel (in ppm)
(Note: The single value shown is the mean of the data set; the range is shown in parenthesis. *ND* – Not detected; *NA* – Not available; *NR* - concentrations not reported due to "analytical difficulties")

	Used Oil							Distillate Fuel*	Residual Fuel*
	Grimmer *et al.* 1981			Pruell & Quinn 1988	Upshall *et al.* 1993	Brinkman & Dickson 1995	Meinz *et al.* 2004	Potter and Simmons, 1998	Potter and Simmons 1998
	Passenger Gasoline	Passenger Diesel	Truck Diesel						
Acenaphthene					3.7	7 (ND – 171)			
Acenaphthylene					1.5	2 (ND – 134)			
Anthanthrene	5.6 (1.6 – 10.8)	1.3 (0.5 – 4.4)	0.4 (0.02 – 0.12)						
Anthracene				34 (25-47)	22	9 (ND – 127)		58 (0.03-200)	50
Benzo[a]anthracene				36 (28-47)	38	65 (ND – 726)**		0.96 0.02-6.7)	550 (29-1500)
Benzo[b]fluoranthene						9 (ND – 93)			
Benzo[k]fluoranthene						6 (ND – 111)			
Benzofluoranthenes [b+j+k]	26.4 (5.7 – 44.3)	5.0 (1.8 – 16.8)	0.51 (0.26 – 1.30)		46				
Benzo[b+k]fluoranthene								0.31 (0.0031-1.9)	440
Benzo[b]naphtho[2,1-d] thiophene	NA	2.2 (0.7 – 4.3)	1.89 (0.78 – 6.20)						
Benzo[ghi]perylene	48.1 (4.4 – 85.2)	4.8 (2.1 – 16.0)	0.33 (0.20 – 0.78)		72	20 (ND – 193)		0.12 (0.0091-0.4)	
Benzo[e]pyrene	30.6 (6.4 – 48.9)	3.7 (1.3 – 10.7)	0.43 (0.23 – 1.10)	11 (ND-27)	32			0.38 (0.054-2.4)	10

* Chemical constituent data presented here are for either residual or distillate fuels, since no constituent data specifically for bunker fuel (residual/distillate blends) were found.
** Range and mean are for benzo[a]anthracene + chrysene

Table 5, continued. Concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) in Used Oil, Distillate Fuel and Residual Fuel Oil (in ppm)

	Used Oil							Distillate Fuel*	Residual Fuel*
	Grimmer et al. 1981			Pruell & Quinn 1988	Upshall et al. 1993	Brinkman & Dickson 1995	Meinz et al. 2004	Potter and Simmons, 1998	Potter and Simmons, 1998
	Passenger Gasoline	Passenger Diesel	Truck Diesel						
Benzo[a]pyrene	18.4 (5.2 – 35.1)	4.0 (0.7 – 11.9)	0.22 (0.13 – 0.60)	9 (ND-22)	15	10 (ND – 65)		2.2 (0.05-8.4)	44
Chrysene				61 (49-85)	45			0.45	690 (29-3100)
Chrysene + Triphenylene	34.0 (8.7 – 74.0)	17.1 (5.1 – 42.8)	2.36 (1.60 – 6.10)						
Coronene	16.6 (2.8 – 29.4)	1.5 (0.1 – 6.4)	0.08 (0.02 – 0.13)						
Dibenz[ah]anthracene					1.5	8 (ND – 94)			
Fluoranthene	46.9 (3.4 – 109)	13.3 (1.3 – 58.9)	0.93 (0.18 – 2.90)	78 (70-91)	55	308 (ND – 2,826)		58 (0.0068-200)	240
Fluorene				83 (42-109)	67	21 (ND – 304)			
Indeno[1,2,3-cd]pyrene	7.9 (2.1 – 12.5)	2.5 (0.8 – 9.0)	0.12 (0.06 – 0.28)		14	4 (ND – 77)		0.16 (0.0064-0.97)	100
Naphthalene				1,910 (854-2520)	52	196 (ND – 1,443)	677 (198 – 1,270)	2600 (100-8000)	42 (2.1-150)
Perylene	5.1 (1.9 – 10.0)	0.7 (0.4 – 2.7)	0.15 (0.11 – 0.35)		1.1				22
Phenanthrene				159 (99-193)	200	81 (ND – 1,387)		880 (0.27-3000)	210 (21-480)
Pyrene	101.5 (5.7 – 326)	20.0 (1.4 – 78)	1.71 (0.33 – 6.40)	88 (80-96)	120	357 (ND – 1,859)		46 (0.18-150)	23

* Chemical constituent data presented here are for either residual or distillate fuels, since no constituent data specifically for bunker fuel (residual/distillate blends) were found.

Table 6. Concentrations of Volatile Organic Compounds in Used Oil, Distillate Fuel and Residual Fuel (in ppm)
(Note: The single value shown is the mean of the data set; the range is shown in parenthesis. *ND* – Not detected; *NA* – Not available; *NR* - concentrations not reported due to "analytical difficulties")

	Used Oil			Distillate*		Residual Fuel*
	USEPA 1984	Brinkman & Dickson 1995	Meinz et al. 2004	No. 2 Fuel Oil Potter and Simmons, 1998	No. 2 Diesel Potter and Simmons, 1998	
Aromatic & Alkyl Aromatic						
Benzene	961 (ND - 55,000)		54 (22-28)	290 (26-1000)		<NO DATA**> ↓
Toluene	2200 (ND - 55,000)		658 (244 – 1200)	1800 (69-7000)	620 (250-1100)	
Xylenes (o-, m- and p- isomers)	3386 (ND - 139,000)		722 (216 –1580)	5000***	2300 (1500-4300)	
Ethylbenzene			241 (104-371)	680 (70-2000)	350 (280-400)	
n-Propylbenzene			135 (74-194)			
Isopropylbenzene			26 (14-39)			
1,2,4-Trimethylbenzene			998 (618-1520)	1800 (900-2400)		
1,3,5-Trimethylbenzene			266 (163-420)			
n-Butylbenzene			86 (39-115)	380 (310-460)		
Sec-Butylbenzene			20 (11-32)			

* Chemical constituent data presented here are for either residual or distillate fuels, since no constituent data specifically for bunker fuel (residual/distillate blends) were found.
** Although no data were found, these substances would not be expected to occur in distillate fuel because they do not occur naturally in petroleum. They occur in used oil generally as a result of illegal or negligent handling practices.
*** Sample size = 1

Table 6, continued. Concentrations of Volatile Organic Compounds in Used Oil, Distillate Fuel and Residual Fuel (in ppm)

	Used Oil			Distillate*		Residual Fuel*
	U.S. EPA 1984	Brinkman & Dickson 1995	Meinz et al. 2004	No. 2 Fuel Oil Potter and Simmons, 1998	No. 2 Diesel Potter and Simmons, 1998	
Chlorinated organic compounds						
Methylene chloride	2800 (ND - 110,000)	ND* (ND – 12)	10 (ND – 83)	<NO DATA**> ↓	<NO DATA**> ↓	<NO DATA**> ↓
1,1,1-Trichloroethane	1388 (ND - 26,000)	78 (ND – 887)				
Tetrachloroethanes (all isomers)						
Trichloroethylene		2 (ND – 59)	ND			
Tetrachloroethylene	1421 (ND - 32,000)	63 (ND – 881)	ND			
o-Dichlorobenzene		1* (ND – 42)	ND			
m-Dichlorobenzene		ND* (ND – 7)	ND			
p-Dichlorobenzene		ND* (ND – 14)	ND			
1,2,4-Trichlorobenzene		1 (ND – 60)				
Trichlorobenzene (all isomers)		ND (ND – 14)				
Chlorofluorocarbons						
Trichlorofluoromethane		5 (ND - 105)				
Dichlorodifluoromethane	373 (ND - 2,200)		ND			
Trichlorotrifluoroethane	62936 (ND - 550,000)	3 (ND – 66)				

* Chemical constituent data presented here are for either residual or distillate fuels, since no constituent data specifically for bunker fuel (residual/distillate blends) were found.

** Although no data were found, these substances would not be expected to occur in distillate fuel because they do not occur naturally in petroleum. They occur in used oil generally as a result of illegal or negligent handling practices.

4.2.4 Discussion

Table 4 - Regulated Chemicals

The specified levels for the regulated chemicals in recycled oil (Health and Safety Code Section 25250.1) were in large part adopted by California based on U.S. EPA regulations. In setting specifications, U.S. EPA concluded that used oil containing chemicals meeting the limits would "not pose hazards significantly greater than virgin fuel when burned." These 1991 specification levels were based on the assessment of possible human health effects that might occur from exposure to these contaminants of concern in an "urban burning scenario" (U.S. EPA, 1991).

The levels of regulated chemicals in used oil and in marine fuels were compared. The data show that:

- Levels of PCBs (< 5 ppm) and halogens (<350 ppm and < 234 ppm in gasoline engine and diesel engine crankcase oil, respectively) reported in the Vermont study were below the limits of detection. In marine fuels, the occurrence of PCBs is highly unlikely, and any halogens should be non-organic (i.e., salts).

- In general, the average concentrations of arsenic, cadmium, chromium and lead in used oil, diesel ("distillate fuel") and residual oil did not exceed regulatory specifications. Except for arsenic, however, the maximum metal concentration detected in used oil samples frequently exceeded regulatory limits. Arsenic in new and used oils is frequently reported as "not detected" (ND), "not reported" (NR), or below the detection limit. According to Sivia *et al*., analyzing for arsenic in used oil can be particularly difficult due to interference problems. They also reported that the method used to prepare used oil samples for analysis can have a profound effect on the analytical results for metals, and that historical data may have underestimated levels of metals in used oil due to inefficiency in the sample preparation methods (Sivia *et al*., 1998).

- The levels of cadmium, chromium, and lead in used oil were generally higher, by an order of magnitude or more, than levels in distillate or residual fuel. Lead levels in the used oil samples were notably higher than levels in marine fuels. Average lead values reported for used oil are highly variable (ND – 265 ppm), and appear to be influenced by outliers. Although no trend can be established with the average lead values reported in the studies presented in Table 4, the maximum concentrations generally decreased over the period from 1995 to 2004.

  The decrease in lead levels in used oil probably reflects the impact of U.S. EPA's Lead Phasedown Program, which began imposing restrictions in the lead content in gasoline in 1973. Greater lead reductions occurred in the 1980s due to an economic incentive program for the refineries. The levels currently detected in used oil may reflect the presence of lead deposits in the engines of older vehicles in the fleet. Today's used oil pool is likely to have even lower levels of lead with the continuing retirement of older vehicles and the cessation of the use of lead as a gasoline additive. However, used oil from aircraft engines remains a source of lead in the used oil waste stream, since aviation fuels still contain tetraethyl lead.

Table 5 – Polycyclic aromatic hydrocarbons

- The data show no clear pattern of differences in the types or concentrations of PAHs in used oil compared with distillate fuel. A single study examined the PAH content of residual fuel (Potter and Simmons, 1998). Except for naphthalene and pyrene, PAH levels in residual fuel were higher than, or comparable to, levels detected in used oil.

- The results of the Pruell and Quinn study (1988) showed significantly higher levels of *naphthalenes* and *phenanthrenes* in used crankcase oil relative to the other PAHs. Naphthalene is likely to have migrated from gasoline into the lubricating oil.

- One study (Brinkman and Dickson, 1995) found PAH levels to be similar across sample types (i.e., used oil samples from vehicle crankcases, storage tanks at quick lube service centers, a recycling facility, a feedtank at a re-refinery, and industrial sources). This observation did not apply, however, to *fluoranthene* and *pyrene*, which were found at very low levels in used industrial oils compared to automotive oils. The authors speculated that these two PAHs might originate from crankcase oil additives.

Table 6 – Volatile Organic Compounds

- Benzene, toluene and xylene levels were significantly higher in used oil samples from the 1984 U.S. EPA study than from the 2004 Meinz *et al*. study. Because the likely source of these compounds is the fuel, the data may reflect differences in the fuel formulation; changes in engine technology may also be factor.

- The benzene levels in used oil reported in the 2004 Meinz *et al.* study were significantly lower than the levels reported in No. 2 fuel oil. However, the maximum benzene level in used oil from the 1984 U.S. EPA study was more than 50-fold higher than the maximum level reported for No. 2 fuel oil. Toluene levels in used oil were within the range reported for levels in No. 2 fuel oil. Xylene levels in used oil reported in the 2004 Meinz *et al.* study were 3- to 7-fold lower than the average reported for No. 2 fuel oil and No. 2 diesel; however, the 1984 U.S. EPA data set for used oil showed average xylene levels that were comparable to levels detected in the distillates. Ethylbenzene concentrations reported in the Meinz et. al study were also comparable to the levels detected in the distillates.

- The levels of chlorinated solvents in the 1984 U.S. EPA study were significantly higher than the levels found in later studies. This reinforces the general consensus among those involved in used oil management that the presence of chlorinated solvents in used oil is largely a result of mismanagement. The decline in the concentrations of these contaminants in the more recent data sets along with the highly variable occurrence observed by Brinkman and Dickson appear to support this conclusion.

Summary

A number of studies have been conducted over the past 30-40 years examining the chemical composition of used oil. As a result, the concentrations of various metals,

chlorinated solvents and organics (particularly PAHs) are better characterized in used oil than in distillate or residual fuel. In a summary table prepared in 1998 by the Petroleum Working Group, the concentrations of non-aromatic hydrocarbons, metals, and PAHs detected in No. 6 Fuel Oil (the primary constituent of bunker fuel) were based primarily on three or fewer studies ("data points"). Data for just two metals (vanadium and nickel) were provided, and these data were derived from a single study. The most complete data set for trace elements in marine fuel oil was generated in a 1995 study conducted by Lloyd's Register (see Appendix B), although these data reflect analytical results from just three samples.

In general, the levels of arsenic, cadmium, chromium and lead measured in used oils were within an order of magnitude (greater or less than) the levels found in residual fuel, the main component of bunker fuel (Table 4). With respect to these four regulated metals, the concentrations of lead represented the greatest difference between used oil and residual fuel (13.2 to 57 ppm in used oil *vs*. 3.5 ppm in residual oil). It is likely that lead levels in used oil from motor vehicles will continue to decline as older trucks and automobiles are removed from commerce. However, it should be noted that aircraft still use leaded fuel and remain a continuing source of lead in the used oil pool.

Vanadium levels in used oil are typically below 3 ppm, while concentrations reported in residual oil are at least an order of magnitude higher (Appendix B). Similarly, the concentrations of nickel detected in used oil are significantly lower than the levels reported in residual oil. These data suggest that addition of used oil to bunker fuel would slightly reduce emissions of vanadium and nickel from marine vessels.

Except for naphthalene and pyrene, the PAH concentrations in residual fuel were similar to, or greater than, the concentrations detected in used oil (Table 5). The concentrations of benzo(a)anthracene, chrysene and indeno[1,2,3-cd]pyrene were all approximately one order of magnitude higher in residual fuel than in used oil.

Based on the 2004 data from Meinz et al., the levels of benzene, toluene, ethylbenzene and xylene in used oil were less than half the levels reported in No. 2 fuel oil (Table 6). VOC data for residual oil were not available, but significant concentrations of VOCs would not be expected in a petroleum mixture with a boiling range of 350-700°C. Hence, if used oil were to be used in place of No.2 fuel oil in bunker fuel, the concentrations of the most hazardous VOCs (benzene, toluene, ethylbenzene and xylene) would all be reduced in the final blend.

4.3 Characterization of combustion products

4.3.1 Emissions from burning used oil

OEHHA was unable to identify any studies characterizing the emissions from the combustion of used oil in marine fuels. This is not surprising in view of the fact that the volume of used oil added to bunker fuel has never accounted for more than a very small percentage of the total fuel consumed by a ship. The data available on hazardous constituents in emissions from the combustion of used oils are generally limited to combustion in small boilers or space heaters. These emissions would differ both qualitatively and quantitatively from emissions generated from a large Category 3 marine vessel engine.

The most cited study of used oil combustion measured total halogens, particulates, arsenic, cadmium, chromium, lead and PCB emissions from small waste oil furnaces with little or no emissions controls (Vermont Agency of Natural Resources, 1996). These contaminants were also analyzed in emissions from the combustion of new engine oil and fuel oils. The testing showed that emissions from used oil combustion have higher levels of most of the contaminants, particularly lead and zinc, than fuel oil.

Compared to marine fuels, used oil contains higher levels of 2- and 3-ring PAHs (naphthalene and phenanthrenes). However, since PAHs may be generated or destroyed by combustion of the fuel, the PAH content of emissions may not necessarily reflect their concentration in the fuel.

The presence of chlorine in used oil is a potential concern because combustion may lead to formation of toxic organochlorine compounds, particularly polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). A study conducted by Huntzinger *et al*. (1991) demonstrated that the halogenated compounds present in modern lubricants do not contribute to PCDD and PCDF formation in internal combustion engines (Hewstone, 1994). It is also reported that the majority of chlorinated organic compounds in used oil are destroyed during combustion in commercial boiler systems. The possible formation of PCDDs and PCDFs as a result of used oil combustion in other devices (e.g., space heaters or marine engines) remains an unresolved issue.

4.3.2 Emissions from burning bunker fuel

As noted previously, the hazardous constituents emitted from burning bunker fuel must be characterized and quantified (i.e., airborne concentrations estimated) in order to assess possible health effects from ship exhaust. For purposes of risk assessment, the constituents of primary concern in marine vessel exhaust include oxides of sulfur and nitrogen, uncombusted or partially combusted hydrocarbons, metals, particulates and “micropollutants” (Lloyd's Register Engineering Services, 1995). The hydrocarbon fraction represents a myriad of organic compounds that may be present in either vapor or particulate phases and which can redistribute between the two phases via evaporation or other processes. The particulate fraction includes a mixture of inorganic and organic substances largely comprising carbon, ash minerals and heavy metals and a variety of hydrocarbon components of the fuel and lubricating oils. Micropollutants are those contaminants present in trace quantities (i.e., parts per billion level or less) that are considered highly toxic, such as carcinogenic PAHs, PCDDs and PCDFs.

4.3.2.1 Lloyds Register marine emissions research

Most marine emissions studies have focused on measuring criteria air pollutants (e.g., NOx, SOx, ozone, carbon monoxide) because of concerns regarding acidification of rain, global warming and respiratory effects resulting from exposure to these pollutants. The exception is a 1995 study published by Lloyd’s Register characterizing emissions of PAHs, nitro-PAHs, PCDDs and PCDFs. With regard to PCDDs and PCDFs, the predominant species detected as emissions from ships burning fuel oil were octachlorodibenzodioxin, 2,3,4,7,8-pentachlorodibenzofuran, 1,2,3,7,8,9-hexachlorodibenzofuran, 2,3,4,6,7,8-hexachlorodibenzofuran, and 1,2,3,4,6,7,8-heptachlorodibenzofuran.

The Lloyd's Register study also evaluated emissions of PAHs and nitro-PAHs. Emissions of nitro-PAHs were consistently low, ranging from non-detect to < 2 micrograms per cubic meter ($\mu g/m^3$). The predominant PAHs emitted from four vessels burning fuel oil were 3- and 4-ring species: phenanthrene, fluoranthene, triphenylene and pyrene. Total PAH emissions ranged from 20.9 to 138.2 $\mu g/m^3$, and emissions were generally higher in vessels running at a higher maximum continuous rating (MCR), a measure of load. Emissions of total PAHs were extrapolated to a worldwide annual estimate assuming a fuel consumption rate of 100 million tonnes per year; total PAH emissions from marine vessels were estimated to be 275 tonnes annually. By comparison, total emissions of PAHs in the Netherlands were estimated to be 1,200 tonnes in 1988.

Emissions of metals were estimated by assuming that the metal content of the emissions was equivalent to the metal content of the fuel burned "…since there is no significant alternative pathway by which these elements can exit from the engine system." Annual metal emissions for 12 heavy metals were estimated and compared to total worldwide anthropogenic emissions. In most cases, marine industry emissions did not exceed 1 percent of worldwide anthropogenic emissions. However, emissions of nickel and vanadium represented 5.5 percent and 4.5 percent, respectively, of worldwide anthropogenic emissions. Available data suggest that the concentrations of these metals in used oil are at least one order of magnitude lower than the concentrations reported in marine fuel oil, so addition of used oil to bunker fuel would be expected to reduce – albeit slightly – their emissions.

It is important to note that the 1995 Lloyd's Register study was termed a "preliminary evaluation" by its authors, who concluded that "…limitations of the data on account of the small sample size and various analytical constraints were acknowledged and further work will be required to confirm initial findings."

4.3.2.2 A.P. Moeller-Sine Maersk marine emissions study

A 2004 study of marine vessel emissions was conducted by MAN B&W Diesel A/S (Copenhagen), in cooperation with CARB, the Port of Los Angeles, the U.S. Maritime Administration, and the University of California. The tests were performed to provide data on the impact of a voluntary "vessel speed reduction" program instituted by the ports of Los Angeles and Long Beach (A.P. Moeller, 2004).

Emissions from both the main engine (Hitachi 12K90MC mk.6, built in 1998) and an auxiliary engine (Holeby 7L32/40) were tested. Fuel for the both engines was ISO (International Organization for Standardization) grade HFO (heavy fuel oil), containing 2.4 percent sulfur and 0.48 percent nitrogen. Main engine emissions were measured individually at engine loads of 85, 75, 50, 25 and 12 percent. Measured emissions included oxides of sulfur and nitrogen, carbon monoxide, carbon dioxide, sulfur dioxide, benzene, and ammonia. In addition, emissions of organic and inorganic acids, alcohols, aldehydes, saturated and unsaturated straight-chain hydrocarbons, and substituted monoaromatic compounds were determined. Emissions of oxides of nitrogen ranged from 20.3 to 24.2 grams per kilowatt-hour (g/kWh); highest emissions were observed at the two lowest engine loads. Emissions of carbon monoxide and hydrocarbons (as methane) were also inversely related to engine load. In contrast,

particulate emissions, which ranged from 1.36 to 1.97 g/kWh, were highest at the two highest engine loads.

4.4 Emission factors and characterization of risk

As discussed in section 4.1.1, constituent-specific emission factors are needed to estimate airborne concentrations that can be used to determine exposure and risk. U.S. EPA and CARB are responding to the fact that oceangoing ships, harbor tugs and commercial boats are major sources of emissions at our ports. Both agencies have programs that monitor ship exhaust and have derived emission factors for a number of criteria air pollutants, including NO_2, SO_2, CO_2, and particulate matter. Emission factors do not exist for other constituents of interest, namely the organic compounds (e.g., PAHs, dioxins), which are necessary for a risk assessment addressing marine fuel emissions (see Section 4.1.2).

Adopting a single emission factor to characterize emissions from marine vessels is an extreme oversimplification because emissions vary according to the size and type of engine and the type of fuel burned, as well as the engine load and speed. Furthermore, abrupt transitions from low to high load conditions can result in very high transient peak values for certain types of emissions, particularly total hydrocarbons and carbon monoxide. The influence of some of these variables on emissions was examined in a 1995 Lloyd's Register study (Lloyd's Register, 1995).

In summary, there are insufficient data available for relating emissions of hazardous constituents from marine vessels to the chemical composition of the fuel they burn. Consequently, a traditional assessment of incremental health risks that may be posed to supplementing bunker fuel with used oil is not possible. Potential health risks posed by changes in the emissions of organic chemicals such as PAHs cannot be assessed because these compounds are present in the original fuels, but they are also destroyed and created *de novo* by the combustion process. Potential health risks posed by metals may be estimated based on the assumption that the mass of metals emitted is equivalent to the mass of metals present in the fuel. Therefore, *for metals only*, the incremental risks associated with addition of used oil to marine fuel oil would be directly proportional to the incremental changes in the concentrations of metals in the blended fuel.

4.5 Characterization of health risks from adding used oil to bunker fuel

The following summarizes why OEHHA is currently unable to conduct a health risk assessment that addresses the additional risk from burning used oil added to bunker fuel.

<u>Lack of fuel constituent analytical data</u>
A primary objective of this report was to compare exposure estimates (and ultimately risk) from burning bunker fuel alone with a blend of bunker fuel and used oil. As discussed in section 4.1, for many hazardous constituents reported to be present in used oil and marine fuels, analytical data providing chemical concentrations are not available. Most of the used oil and marine fuels studies focus on analyzing for the regulated constituents (arsenic, cadmium, chromium, lead, halogens, and PCBs) or those that may affect the performance of the ship engine. Because all hazardous constituents in used oil and in bunker fuels have not been adequately characterized, it

follows that contaminants (including byproducts of combustion) in marine emissions cannot be fully characterized.

Lack of emission factors

The lack of knowledge of the full array of contaminants in emissions resulting from burning used oil and marine fuels represents an area of uncertainty that precludes a comparative risk assessment. Even if comprehensive hazardous constituent data were available, the levels of hazardous constituents in emissions still cannot be quantified because emission factors have not yet been generated for many contaminants. Consequently, exposure point concentrations for the full array of hazardous constituents in used oil (and in marine fuels) cannot be calculated.

Apparent negligible effect of adding used oil to bunker fuel

With the possible exception of lead and two PAH compounds, the data in Tables 4 - 6 do not show clear differences in the composition of hazardous constituents in used oil and residual fuels. As noted earlier, when bunker fuel was supplemented with used oil in the past, the latter was added at about 1 to 3 percent of the total fuel volume. Since the compositional differences that may occur in used oil and residual fuels would be masked by this high dilution rate, any potential incremental health impacts would likely be small.

5.0 USED OIL IN MARINE FUELS: THE OUTLOOK

5.1 Marine fuel regulations

In an effort to address air pollution for ships, regulations have been developed at the State, federal and international levels. The new regulations, along with revised industry specifications, are likely to result in significant changes in the nature of marine fuels. These changes, in turn, have the potential to impact the markets for used oil or recycled oil in the next decade.

5.1.1 International regulations

5.1.1.1 International Convention for the Prevention of Pollution from Ships (MARPOL) Annex VI

The United Nations' International Maritime Organization (IMO) was established to promote shipping safety and to reduce pollution from all aspects of marine vessel operation. To help achieve these goals, the IMO develops and adopts international treaties called "conventions," which set up legal frameworks for regulating maritime safety and ship-derived environmental pollution. When a government accepts an IMO Convention, it agrees to make it part of its own national law (IMO, 2004a).

The International Convention for the Prevention of Pollution from Ships, more commonly referred to as MARPOL, is the main international convention covering prevention of pollution of the marine environment by ships from operational or accidental causes. It covers pollution by oil, chemicals, harmful substances in packaged form, sewage and garbage. MARPOL is a combination of two treaties adopted in 1973 and 1978, and has been updated by amendments through the years (IMO, 2004b).

The MARPOL convention consists of six annexes. Annex VI, Regulations for the Prevention of Air Pollution from Ships, was adopted in 1997, and will enter into force on May 19, 2005. Annex VI sets limits on emissions of nitrogen oxides (NOx) from ship exhaust and prohibits deliberate emissions of ozone depleting substances. It establishes a global sulfur cap of 4.5 percent (45,000 ppm) for fuels used onboard ships, and requires that the fuel not include any "added substance or chemical waste which…jeopardizes the safety of ships or adversely affects the performance of the machinery, is harmful to personnel, or contributes overall to additional air pollution." It also contains provisions for designating SOx "emission control areas" with more stringent controls on sulfur emissions (where ships must use fuel containing not more than 1.5 percent sulfur, or use control devices to reduce SOx emissions). MARPOL Annex VI does not place international restrictions on particulate matter (PM), hydrocarbon or carbon monoxide emissions from marine vessels (IMO, 2004b).

5.1.1.2 Commission of the European Community

The European Community is attempting to take more aggressive steps towards reducing atmospheric emissions from the shipping industry. Their primary concern is curbing emissions of SO_2 and NOx because of the damaging human health and environmental effects resulting from acidification, ground level ozone and particulate matter. In 1999, the European Council set forth Directive 1999/32/EC, which sets a 0.2 percent (2,000 ppm) sulfur limit for marine distillate fuels used by ships in inland waterways and territorial waters (within ~12 miles from shore) (Council of the European Union, 1999).

The European Council has not established directives for limiting sulfur in residual bunker fuels that are used out in the open sea. A 2002 study that quantified ship emissions in European seas and port areas projected that by 2010, ship emissions of SO_2 will exceed 75 percent of all land-based emissions (Committee on Oil in the Sea, 2003). In response, the European Council has proposed modifications to the 1999/32 Directive that would require 1.5 percent sulfur limits for marine fuels used by all seagoing vessels in areas of northern Europe and for passenger ships on regular services to or from European Community ports (Commission of the European Communities, 2003).

5.1.1.3 International Council on Combustion Engines (Conseil International des Machines à Combustion)

The International Council on Combustion Engines (more commonly referred to as CIMAC, the acronym for its French name, *Conseil International des Machines à Combustion*) is a global nonprofit organization that provides technical and scientific information in the field of internal combustion engines, particularly heavy-duty diesel engines. The CIMAC Heavy Fuels Working Group makes recommendations regarding fuel requirements for diesel engines. CIMAC's recommendations serve as technical input to the International Organization for Standardization's (see section 5.1.1.4) standards-setting process for fuels.

In June 2003, the CIMAC Heavy Fuel Oil Working Group updated its recommendations concerning fuel quality for diesel engines (CIMAC HFO Working Group, 2003). Among the working group's recommendations are the incorporation of the future lower global

limits for sulfur and a prohibition on the blending of used oil in marine fuel. This recommendation is based on evidence that used oil can have adverse effects on engine performance, and that the fuel may provide a route for chemical waste (e.g., industrial solvents) to enter the bunker fuel pool.

In order to prevent the addition of used oil to marine fuels, the fuel recommendations contain limits on “fingerprint” elements indicative of the presence of used oil, as follows: 15 ppm (μg/g) for zinc, 15 ppm for phosphorus, and 30 ppm for calcium. These elements are used in detergent and anti-wear additives in lubricating oil. If all three elements are present in amounts exceeding their respective limits, this indicates that used oil has been blended into the fuel.

5.1.1.4 International Organization for Standardization (ISO)

The ISO is a non-governmental organization that is a network of national standards institutes from148 countries. ISO develops consensus agreements among national delegations representing suppliers, users, government regulations, consumers and other interest groups. These agreements define specifications and criteria to be applied consistently in the classification of materials, in the manufacture and supply of products, in testing and analysis, in terminology and in the provision of services. In this way, the standards provide a reference framework, or a common technological language, between suppliers and their customers, facilitating trade and the transfer of technology (ISO, 2004).

In 1987, in response to the demand of the marine and petroleum industries for standardization of marine fuel quality, ISO introduced the first international standard for marine fuel. This standard, ISO 8217, which was revised in 1996, specifies 11 parameters for residual fuels and 14 parameters for distillate fuels. These parameters include viscosity, density, carbon residue, ash content and percent sulfur (Vis, 2003a).

A work group of ISO is in the process of revising ISO 8217 (Secretariat of ISO/TC 28/SC4, 2002). It is anticipated that, in addition to ensuring conformance with the new sulfur limits specified in MARPOL Annex VI, these revisions will include a provision to curb the (albeit limited) practice of adding used oil to bunker fuel (Lloyd's List, 2001).

5.1.2 U.S. federal regulations

Air pollution from ship engines can be reduced in two ways: either by designing engines to be less polluting, or altering the fuel to be cleaner burning. The U.S. EPA has passed vessel regulations for both reduction measures.

5.1.2.1 Engine standards

In 2003, U.S. EPA for the first time adopted national emission standards for new marine diesel engines that will be installed on vessels flagged or registered in the United States (U.S. EPA, 2003b). These vessels use the largest marine engines, referred to as “Category 3” engines. Under this rule, new engines built in 2004 or later for U.S.-flagged ships would be subject to the MARPOL Annex VI 1997 standards for NOx. U.S. EPA acknowledges in their regulatory support document that these standards would be achieved almost immediately, because manufacturers have already been

certifying to these standards under a voluntary program since 2000. There are also rules for Category 1 and 2 engines.

5.1.2.2 Diesel fuel standards

Federal off-road diesel fuel used for all non-road engines (including locomotive and marine engines) currently contains about 0.3 percent (3,000 ppm) sulfur. U.S. EPA recently adopted the Clean Air Non-road Diesel Rule, which will require reductions in the sulfur content of diesel fuel for locomotive and marine uses to 0.05 percent (500 ppm) starting June 2007, and further to 0.0015 percent (15 ppm) starting 2012 (U.S. EPA, 2004b).

The new rule, which covers only U.S.-flagged vessels, applies to all No.1 and No. 2 distillate fuels used or intended to be used in marine diesel engines. The rule does not apply to distillates used for stationary diesel engines, industrial boilers, or for heating. It also excludes fuels heavier than a No. 2 distillate, or any distillate fuel with a T-90 distillation point greater than 700°F, when used in Category 2 or 3 marine engines. Hence, Number 4, 5, and 6 fuels (e.g., IFO Heavy Fuel Oil Grades 30 and higher), as well as fuels meeting ASTM specifications DMB, DMC, and RMA-10 and heavier are not affected by the new rule (U.S. EPA, 2004b).

The U.S. EPA estimates that non-road diesel equipment covered by the new rule currently accounts for 47 percent of diesel particulate matter and 25 percent nitrogen oxides from mobile sources nationwide. The lower sulfur fuel will provide immediate public health benefits by reducing PM from engines in existing non-road equipment. It also makes it possible for engine manufacturers to use advanced clean technologies, similar to catalytic technologies used in passenger cars (U. S. EPA, 2004a).

In California most diesel fuel used by off-road sources already meets the 500 ppm standard, and the CARB is expected to propose a rule in May 2005 requiring the use of 15 ppm CARB diesel by name in 2007 (5 years prior to the U.S. EPA non-road marine regulation) (see Section 5.1.3).

5.1.2.3 Prohibition against used oil in marine fuel

Another provision of the Clean Air Non-road Diesel Rule is the prohibition on the use of used oil (or diesel fuel containing used oil) in the fuel delivery systems of non-road equipment engines manufactured in model year 2011. The prohibition applies to used oil that has not been re-refined. In its rulemaking document, U.S. EPA refers to practices such as blending used motor oil directly into the equipment fuel tank, blending it into the fuel storage tanks, and blending small amounts of motor oil from the engine crankcase into the fuel system as the equipment is operated (U. S. EPA, 2004b). Motor oil normally contains high levels of sulfur (3,000 to 10,000 ppm), and would impair the sulfur sensitive emission control devices. Further, depending on how the oil is blended, it could increase the sulfur content of the fuel by as much as 200 ppm. The U.S. EPA is also requesting that lubricant additives be reformulated to contain less sulfur.

5.1.3 California regulations

The California Air Resources Board (CARB) is evaluating options for addressing air quality issues and concerns relating to maritime activities in California. Particular emphasis is on the reduction of the air pollutants NOx, SOx, and diesel particulate matter from commercial marine vessels operating in California coastal and inland waters (CARB, 2004b). CARB has convened the Maritime Air Quality Technical Working Group to provide a forum for discussion of air quality issues and concerns pertaining to maritime activities in California. A key task of the group is to participate in the development of emission reduction strategies for commercial marine vessels and dockside equipment (CARB, 2004a).

CARB is exploring emission reductions strategies such as engine design, retrofits, and the use of cleaner fuels. The CARB's cleaner fuel concept for oceangoing ships is to use marine gas oil (MGO, which is also known as DMA) in auxiliary engines at dockside and in California coastal waters instead of using the more polluting heavy (residual) fuel oil.

To address emissions from harbor craft, November 2004 CARB approved a requirement specifying the use of CARB diesel fuel in the engines of these vessels. Currently, harbor craft can use off-road diesel fuel with higher sulfur and aromatics levels compared to California on-road lower sulfur fuel; in practice, they use federal off-road diesel, federal on-road diesel, and California on-road diesel (CARB, 2003). This amendment to the California low sulfur diesel fuel regulations will reduce the maximum sulfur content from 500 ppm to 15 ppm ("ultra-low sulfur") for both on-road and off-road diesel engines starting in mid 2006 (Title 13, California Code of Regulations, Section 2281). Under the CARB's concept, all harbor craft engines will use only California on-road low sulfur diesel and eventually the ultra-low sulfur.

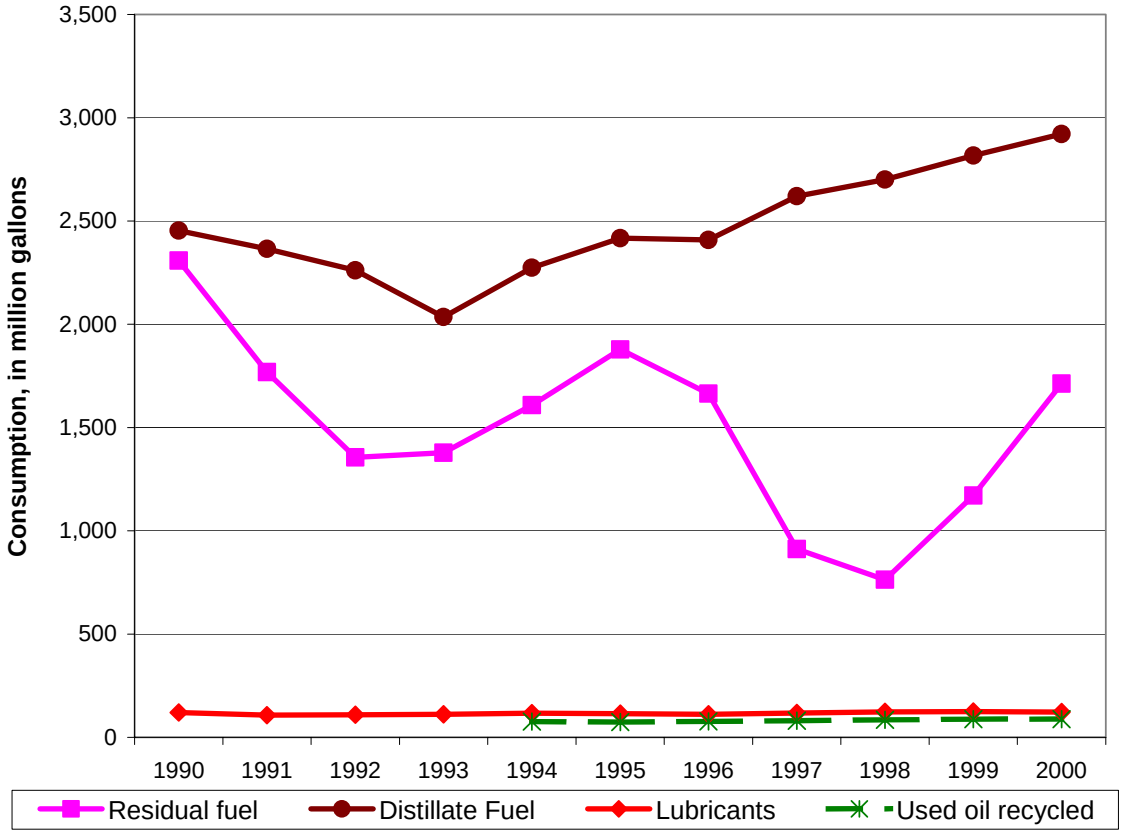
The CARB also is encouraging the U.S. EPA to work with the IMO to create a "sulfur emission control area" along the West Coast under the existing provisions of MARPOL Annex VI. This would ensure that ships either use residual fuel with a sulfur content at or below 15,000 ppm (1.5 percent), or an exhaust gas cleaning system to reduce emissions of sulfur oxides.

5.2 Consumption and demand for marine fuels

Figure 7 presents trends in the volume of residual fuel, distillate fuel oil, and lubricants consumed by the transportation sector in California (Energy Information Administration, 2000a, 2000b). Almost all of the residual fuel consumption by the transportation sector is used for "vessel bunkering" (i.e., commercial or private boats such as pleasure craft, fishing boats, tugboats, and oceangoing vessels). In contrast, only about 5 percent of the total distillate fuel is consumed for marine uses; this amount is almost equivalent to the amount of lubricants consumed. For purposes of comparison, data on the volumes of lubricating and industrial oil recycled in the State from 1994 to 2000 are also plotted on the graph (CIWMB, 2004a). The volume of used oil received by recycling facilities reporting to the CIWMB represents anywhere from 4 to 11 percent of the amount of residual fuel sold in the State, about 3 percent of the amount of distillate fuel, and 75 percent of the amount of lubricant.

The U.S. Department of Energy forecasts that U.S. consumption of distillate fuel will be 2.0 million barrels per day higher in 2025 than it was in 2002 and residual fuel use is projected to increase slightly, mostly for electricity generation (Energy Information Administration, 2004a).

Figure 7. Estimated Annual Consumption of Fuels and Lubricants by the Transportation Sector in California



Sources: Energy Information Administration and California Integrated Waste Management Board

5.3 Marine fuel as a market for recycled oil?

Given the prevailing shipping industry purchasing practices, regulatory changes (MARPOL and U.S. EPA regulations), and revisions to the ISO 8217 marine fuel specifications, it is highly unlikely that used oil or recycled fuel oil will be added to marine fuels in the future. In fact, this practice has not been widespread in the past five years.

The distillate product of used oil recycling – marine diesel oil, or MDO – appears to exhibit properties very similar to the distillate marine fuels DMA and DMB. Table 7 compares properties of used oil-derived MDO to the specifications for marine gas oil (DMA) and marine diesel oil (DMB), per the ISO 8217 standard:

Table 7. Selected Properties of Marine Distillate Fuels (DMA and DMB) and Marine Diesel Oil (MDO) Derived from Used Oil

Parameter	Marine gas oil (DMA) ISO 8217 Specifications [a]	Recycled marine diesel oil (MDO)[b]	Marine diesel oil (DMB) ISO 8217 Specifications [a]
Density at 15°C	0.890	0.880	0.900
Viscosity at 40° C, cSt	1.5 (min) 6.0 (max)	7.28	11 (max)
Sulfur % mass	1.5 (max)	0.3	2.0 (max)
Flash point, (°F)	140°F	150°F	140°F
Ash % (m/m)	0.01 (max)	0.002[c]	0.01 (max)

a. Bunkerworld, 2004a
b. DeMenno/Kerdoon, 2004b; DeMenno/Kerdoon, 2004d
c. Ennis, 2004

Current regulations do not preclude the use of MDO derived from used oil as a marine fuel; U.S. EPA's limit for sulfur in non-road diesel is currently at 0.3 percent. Used oil-derived MDO has, on average, a sulfur concentration of 0.3 percent (3,000 ppm) (DeMenno/Kerdoon, 2004d), consistent with sulfur levels found in new motor oil. This level meets the current ISO 8217 specification for sulfur levels in DMB -- no more than 2.0 percent (20,000 ppm) (Bunkerworld, 2004a). Implementation of the more stringent sulfur limits in the future, however, will impact this market. For example, California has limited diesel fuel sulfur limits to 15 ppm (0.0015 percent) by 2006. Additionally, U.S. EPA's Non-road Diesel Rule has limited sulfur levels in marine diesel fuels used in harbor craft to a maximum of 500 ppm (0.05 percent) beginning in 2007 and 15 ppm (0.0015 percent) in 2012. Sulfur limits specified under current and future State and federal regulations are shown below in Table 8.

Table 8. Sulfur limits for diesel fuel (percent by weight and ppm)

Current Limits		Future Limits		Recycled marine diesel oil
CARB diesel On-road and non-road	U.S. EPA diesel	CA on-road and non-road; EPA on-road Ultra-low sulfur diesel	U.S. EPA non-road diesel	
0.05% (500 ppm)	On-road: 0.05% (500 pm) Non-road: 0.3% (3,000 ppm)	By 2006: 0.0015% (15 ppm)	By 2007: 0.05% (500 ppm) By 2012: 0.0015% (15 ppm)	0.3% (3,000 ppm)

Given its low levels of ash and sulfur and its low viscosity (see Table 9), MDO derived from used oil has value as a blending agent for residual fuel. This use is not likely to be impacted by the lower limits on sulfur levels in the future. International regulations (MARPOL) will require that the intermediate fuels, IFO 180 and IFO 380 (which are a

blend of distillate and residual fuel), contain no more than 4.5 percent (45,000 ppm) sulfur for oceangoing trips by mid-2005. Blending used oil-derived MDO (as the distillate portion of the intermediate fuel) with residual fuels is not likely to increase the sulfur levels of the resultant fuel blend to levels exceeding this limit. Furthermore, this use could create a "supply pull" situation, given the extremely high volume of residual fuel consumed in marine vessels.

Table 9. Selected Properties of Marine Diesel Oil Derived from Used Oil and Residual Fuel Blends

Parameter	Recycled marine diesel oil[a] (DMB)	Residual fuel IFO 180 (RME 25) ISO 8217 Specifications[b]	Residual fuel IFO 380 (RMG 35) ISO 8217 Specifications[b]
Density at 15°C	0.880	0.991	0.991
Appearance	Dark amber to dark brown	Black	Black
Viscosity, cSt	7.28 at 40°C (min)	68 at 50°C 25 at 100°C	340 at 50°C 35 at 100°C
Sulfur, % mass	0.3 (3,000 ppm)	5.0 (50,000 ppm) By 2005: 4.5% (45,000 ppm) (per MARPOL Annex VI amendment)	5.0 (50,000 ppm) By 2005: 4.5% (45,000 ppm) (per MARPOL Annex VI amendment)
Flash point, °F	150 °F (min)	140 °F (min)	140 °F (min)
Ash % (m/m)	0.002	0.1	0.15
Used lubricating oil[c] (ULO), based on: Zinc Calcium Phosphorus		Fuel shall be free of used lubricating oil (ULO). A fuel shall be considered free of ULO if one or more of the elements zinc, phosphorus and calcium are below or at the specified limits. It is required that the content of all three elements exceed the limits before a fuel shall be deemed to contain ULO: Zinc, 15 ppm Calcium, 30 ppm Phosphorus, 15 ppm	

a. DeMenno/Kerdoon, 2004; DeMenno/Kerdoon, 2004d
b. Bunkerworld, 2004a
c. Proposed revisions to ISO 8217
NOTE: More comprehensive tables presenting comparisons among different marine fuels and recycled oil products can be found in Appendix A.

The adoption of new fuel specifications that limit the levels of zinc, calcium and phosphorus (the "fingerprint" elements indicative of the presence of used oil in a fuel) will impact the continued use of fuel oil derived from used oil as a blending agent. Residual fuels typically contain these fingerprint elements at levels significantly lower than the limits in the new specifications (Kassinger, 2004b)

An economically viable option for recycled used oil may be as refinery feedstock. It is unclear, however, whether this process will yield residues (i.e., residual fuel) containing used oil fingerprint elements at levels exceeding specification limits (Kassinger, 2004b). As mentioned in section 2.2.4, the total amount of used oil collected in California in one year is insignificant compared to the amount of feedstock consumed by the State's refineries; for example, all of the used oil collected in 2002 would represent less than two days' worth of refinery feedstock. Because used oil is designated as a hazardous waste in California, any facility that treats used oil – such as a petroleum refinery that uses the material as feedstock along with crude oil -- must possess a hazardous waste facility permit issued by DTSC. By contrast, this requirement for a permit would not apply to a refinery that processes recycled oil meeting the purity standards specified in Health and Safety Code Section 25250.1(a)(3)(B) (see Section 2.1).

6.0 FINDINGS

Used oil management

Used oil is the largest hazardous waste stream in California, making up about one-third of all routinely generated hazardous wastes shipped offsite every year. Not only is it essential that used oil be managed properly to prevent environmental contamination, but also to reclaim a valuable resource, particularly in light of the ever increasing demand for petroleum products and the rising price of crude oil.

Volumes of used oil recycled in California have shown a steady increase over the years. The largest volume end-product of the recycling of California's used oil is fuel oil. For reporting purposes this includes the distillate product marine diesel oil (MDO). Fuel oil made up an average of about two-thirds of the volume of all recycled products annually from 1992 to 2002. There is, however, virtually no market for fuel oil in California because of air pollution issues, and it is largely shipped out of State (Boughton, 2004).

MDO is very similar to the distillates commonly used in today's marine fuels. Given the fact that the production of MDO is distinctly different from the process that yields fuel oil (the latter does not involve distillation), and that the MDO has different uses and, thus, different markets, it would be useful to track the production of used oil-derived MDO separately.

Used oil in bunker fuel

In the past, used oil was added as a supplement to bunker fuel at a very low percentage (1 – 3 percent). However, it appears that this practice is no longer common; in fact, testing conducted by commercial fuel laboratories in the past five years has shown no evidence of the presence of used oil in bunker fuel. This change was apparently the result of a number of widely publicized incidents of bunker fuel contamination that led to significant engine damage. Used oil is perceived by the shipping industry as an avenue for the intentional or accidental introduction of chemicals wastes detrimental to ship engines. Although used oil was not involved in fuel contamination incidents, most shippers nevertheless became unwilling to accept used oil in bunker fuel.

New international (MARPOL) and federal (U.S. EPA) regulations designed to curb air pollution from marine fuels by lowering allowable sulfur concentrations in fuel include a prohibition against the addition of used oil and other chemical wastes into marine fuels. In preparation for the recently enacted MARPOL regulations, the shipping industry has developed specifications (to be adopted as the new ISO standard for marine fuels) that will limit the levels of calcium, phosphorus and zinc in fuels. The presence of all three chemicals in residual fuel above the specified limits is interpreted as evidence of the presence of used oil.

Current regulations do not preclude the use of MDO derived from used oil in marine fuels for smaller vessels (e.g., harbor craft). Although the recently adopted regulations that set more stringent sulfur limits for distillate fuels may impact this market, the use of MDO as a blending agent with residual fuel for use in the main engines of oceangoing ships is not likely to be affected. Given the extremely high demand for residual fuel for marine vessels, this use of MDO as a blending agent would represent a “supply pull” situation, ensuring that a product of used oil recycling is returned to the economic mainstream.

Another possible option for recycling used oil would be to use it as feedstock in the petroleum refining process. A potential obstacle may be the insignificant volume of used oil collected in California compared to the volume of crude oil processed by the State’s refineries. Another obstacle is that the processing of untreated used oil as feedstock may be subject to hazardous waste permitting requirements in California. Nevertheless, it would be worthwhile to examine the feasibility and potential environmental and human health impacts of this option.

Human health implications of adding used oil to bunker fuel

Much of the available analytical data on the composition of used oil are decades old and in all likelihood are no longer relevant given the changes in fuel composition and engine technology. The studies identified for purposes of assessing health risk were conducted over a 28-year period, where each study examined a different spectrum of analytes. During this time, fuel formulations and automobile engine technology evolved significantly. The most obvious change in the composition of used oil during this period was the dramatic drop in lead content that occurred after tetraethyl lead was eliminated from motor vehicle fuel. Methods of oil sample preparation and analysis also improved, suggesting that data from older studies may not accurately reflect true contaminant concentrations. For these reasons, data from these studies are difficult to compare, and trends in contaminant concentrations, if any, are difficult to identify. Similarly, data on the composition of the distillate fuels and residual fuels used in ships are incomplete.

In addition to identifying constituents in used oil and bunker fuel, the hazardous constituents emitted from burning used oil and marine fuels must be characterized and quantified (i.e., airborne concentrations estimated) in order to assess possible health effects from ship exhaust. Constituent-specific emission factors are used to estimate airborne concentrations that can be used to determine exposure and risk. While emission factors have been developed for the criteria air pollutants (i.e., NOx, SOx, CO_2 and particulate matter), they do not exist for other constituents of interest that are necessary for addressing potential health effects resulting from marine fuel emissions.

The limited analytical data for used oil and residual fuels show levels of hazardous constituents of concern – arsenic, cadmium, chromium, lead, and polycyclic aromatic hydrocarbons – within an order of magnitude when comparing used oil and residual fuel. (The levels of lead in today's used oil are likely to be lower than those reported in the studies we reviewed, given the prohibition on the use of lead gasoline additives. However, the continued use of leaded fuel in aircraft provides an ongoing source of lead in the current used oil pool.) Therefore, it is reasonable to expect that addition of used oil to marine fuels at the amounts used in the past (1-3 percent) would not substantially increase the concentrations of hazardous constituents in the resultant fuel. However, within the context of considerable uncertainty regarding the chemical composition of both used oil and bunker fuel and the emissions from combustion, conclusions about the human health consequences of adding used oil to bunker fuels would be premature. Thorough characterization of the hazardous constituents in today's used oils and in today's fuels would allow for the evaluation of health risks associated with different uses of used oil, and assist in the development of strategies that promote more environmentally sound management options.

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APPENDIX A

APPENDIX A
SELECTED PROPERTIES OF
UNUSED LUBRICATING OIL, USED OIL, RECYCLED OIL PRODUCTS, AND MARINE FUELS

			Recycled oil products			Distillate marine fuels		Residual marine fuels	
	Unused motor oil (10W/40)	Used motor oil	Fuel oil cutter	Rerefined lubricating oil	Recycled marine diesel oil (DMB)	Marine gas oil (DMA)	Marine diesel oil (refinery) (DMB)	IFO 180 (RME 25)	IFO 380 (RMG 35)
Boiling point, ^{o}F	650-1000		185-1,040		364				
Density at 15.6^{o}C	0.880	0.885	0.910	0.871	0.880	0.890	0.900	0.991	0.991
Appearance	Amber to dark amber		Dark amber to dark brown	Bright and clear	Dark amber to brown			Black	Black
Viscosity cSt	88.0 at 40°C; 13.5 at 100°C	71 at 37.7^{o}C	42 at 50°C	54 at 40°C; 7.4 at 100°C	7.28 – 12 at 40°C	1.5(min), 6.0(max) at 40°C	11(max) at 40°C	68 at 50°C; 25 at 100°C	340 at 50°C; 34 at 100°C
Bottom solids and water, % vol		19	2.0 (max)		0.25 max				
Sulfur, % mass	0.5	0.29-0.5	0.4-0.5	0.07	0.3	1.5 (max)	2.0 (max)	5*	5*
Flash point (^{o}F)	415 (min)	210 (min)	150 (min)	435 (min)	150 (min)	140	140	140	140
Ash % (m/m)	1	0.65	0.3-0.6	0.001	0.002	0.01 (max)	0.01	0.1	0.15
Zinc (ppm)	1,400	90-1,550	700-900					**	**
Calcium (ppm)			700-1,000					**	**
Phosphorus (ppm)			600-1,200					**	**

* By 2005: 4.50% (max) per MARPOL Annex VI amendment

** Fuel shall be free of used lubricating oil (ULO). A fuel shall be considered free of ULO if one or more of the elements zinc, phosphorus and calcium are below or at the specified limits. It is required that the content of all three elements exceed the limits before a fuel shall be deemed to contain ULO:

Zinc, 15 ppm
Calcium, 30 ppm
Phosphorus, 15 ppm

APPENDIX B

APPENDIX B-1
Composition of Used Oil
Elemental Analysis

	Raymond et al. (1976)[a]		Cotton et al. (1977)[b]		Becker & Comeford (1980)		U.S. EPA (1984)[e]	
	Car Engine	Truck Engine						
	(ug/g)	(ug/g)	Range (ug/g)	Mean (ug/g)	Range A[c] (ug/g)	Range B[d] (ug/g)	Range (ug/g)	Mean (ug/g)
Aluminum	22	10	4 - 41	15	<0.5 - 758			
Antimony								
Arsenic							<0.1 - 100	17.3
Barium	480	36	10 - 693	287.4	9 - 3,906		ND - 3,906	131.9
Beryllium								
Boron	10	ND						
Bromine						1,050 - 2,950		
Cadmium							<ND - 57	3.1
Calcium	700	780	969 - 3,986	1,557	211 - 2,291			
Chlorine					1,700 - 4,700	1,140 - 3,300	<100 - 459,000	4,995
Chromium	21	3	5 - 24	10.6			ND - 690	28.0
Cobalt								
Copper	17	18	6 - 56	28.5				
Iron	260	180	88 - 655	200.7	97 - 2,401			
Lead	7500	75	19 - 13,885	7,079	85 - 21,676	4,770 - 13,110	ND - 21,700	664.5
Magnesium	1600	1100	8 - 999	306				
Manganese	3	ND	1 - 8	3.7				
Mercury								
Molybdenum	10	4						
Nickel	ND	ND	ND - 5	1.3				
Nitrogen								
Phosphorus	1400	1350	81 – 1,393	901	319 - 1,550			
Silicon	18	8	8 - 87	30.2				
Silver	ND	ND	NA	NA				
Sodium	51	39	8 - 660	114.2				
Sulfur					1,700 - 10,900	3,800 - 4,400		
Tin	5	3	ND - 14	4.5				
Vanadium	ND	ND	ND	ND				
Zinc	1500	1300	80 – 2,500	1,061	260 - 1,787		0.5 - 8,610	580.3

[a] Table 2; n = 1 (one sample from each source was analyzed)

[b] Table 4; n = 30

[c] Table 3; data compiled by the authors from 10 reports published between January 1972 and January 1978

[d] data generated by the authors: Tables 32 (S), 37 (Pb), and 39 (Cl and Br)

[e] Table 2 (summary table of data from Tables 15, 16 and 17); n = 537-835

[f] Table 2; n = 1

[g] Table 1; n = 1

	Mumford et al. (1986)[f]	Vazquez-Duhalt & Greppin (1986)[g]	U.S. EPA (1991)[h]		
			Gasoline Engine	Diesel Engine	Storage Tank[i]
	(ug/g)	(ug/g)	Range (ug/g)	Range (ug/g)	Range (ug/g)
Aluminum					
Antimony	25				
Arsenic			<1	2	<2.4
Barium			1 - 43	1.5 - 6.4	11.6 - 32.6
Beryllium					
Boron					
Bromine					
Cadmium	0.1	0.5	0.5 - 3.4	0.7 - 3	1.0 - 5.0
Calcium	347.5				
Chlorine					
Chromium	ND	1	0.8 - 23	1.8 - 7.1	2.67 - 5.0
Cobalt	0.25				
Copper	27.5	6			
Iron	130				
Lead	1075	3092	5.5 - 150	2.9 - 19	29 - 345
Magnesium	115				
Manganese	7.5				
Mercury	ND				
Molybdenum					
Nickel	8.5	0.6			
Nitrogen					
Phosphorus	32,277				
Silicon					
Silver					
Sodium					
Sulfur					
Tin					
Vanadium					
Zinc	265	1129			

[h] Table III.C.3A; n = 12 (gasoline engine), n = 10 (diesel engine), n = 8 (storage tank)

[i] Storage tank samples (automotive fluids and oils) collected for "identification of the extent of any post-use adulteration that occurred"

[j] Table 2-1; number of samples not provided. Data apparently based on samples collected and analyzed in 1982-83.

Published in reports by USEPA (1984) and AD Little (1983)

[k] Reference notes that "lead levels have decreased since these values were determined in 1982 and 1983

	U.S. EPA (1993)[j]		Brinkman & Dickson (1995)[l]		Vermont Agency Nat Res (1996)[m]				Sivia et al. (1998)[n]	Meinz et al. (WA) (2004)[o]	
					Gasoline Engine		Diesel Engine				
	Range (ug/g)	Mean (ug/g)	Range (ug/mL)	Mean (ug/mL)	Range (ug/g)	Mean (ug/g)	Range (ug/g)	Mean (ug/g)	(ug/g)	Range (ug/g)	Mean (ug/g)
Aluminum	2 - 640	45							< 10		
Antimony											
Arsenic	1 - 100	12			NR	NR	NR	NR	< 2.5	ND - 0.45	0.12
Barium	9 - 160	66			ND - 7.0	2.7	2.3 - 5.9	3.4	3.97		
Beryllium					ND	<0.02	ND	<0.02			
Boron											
Bromine											
Cadmium	0.6 - 2.8	1	ND - 5	ND	ND - 3.3	<1.5	0.8 - 6.6	2.4	1.03	ND - 0.86	0.17
Calcium									224		
Chlorine	1,000 - 6,700	2,200									
Chromium	1 - 37	6	ND - 233	10	ND - 4.2	3.2	2.4 - 6.9	3.9	< 5	2.0 - 17.6	4.5
Cobalt											
Copper									280		
Iron	58 - 1,300	240							41.6		
Lead	170 - 2,100[k]	1,100[k]	ND - 265	29	ND - 104	47.2	23.6 - 146	57	42.5	0.2 - 66.1	13.2
Magnesium	5 - 590	260							688		
Manganese											
Mercury											
Molybdenum									4.49		
Nickel					ND - 1.8	<1.4	ND - 3.0	1.9	2.77		
Nitrogen	100 - 2,800	1,000									
Phosphorus											
Silicon											
Silver											
Sodium											
Sulfur	2,700 - 7,500	5,000			2,430 - 4,600	3,600	2,120 - 4,110	2,500			
Tin											
Vanadium	0.1 - 13	3							< 2.5		
Zinc	90 - 1,550	800			867 - 1330	1161	568 - 2370	1114	1240		

[l] Table 5; n = 96

[m] Table 1; n = 21; arsenic concentrations not reported (NR) due to "analytical difficulties"

[n] Table 10; n = 1 (sample 961012; used gasoline auto engine oil)

[o] Range and mean nine samples collected from individual autos + one sample collected from the tank of a commercial oil change business

APPENDIX B-2

Composition of Used Oil
Polycyclic Aromatic Hydrocarbons

	Becker & Comeford (1980)[a]				Grimmer et al. (1981)					
	Composite Auto		Tractor Diesel		Passenger Gasoline[b]		Passenger Diesel[c]		Truck Diesel[c]	
	Range (ug/g)	Mean (ug/g)	Range (ug/g)	Mean (ug/g)	Range (ug/g)	Mean (ug/g)	Range (ug/g)	Mean (ug/g)	Range (ug/g)	Mean (ug/g)
Naphthalene										
Acenaphthylene										
Acenaphthene										
Fluorene										
Phenanthrene										
Anthracene										
Fluoranthene					3.4 - 109	46.9	1.3 - 58.9	13.3	0.18 - 2.90	0.93
Pyrene					5.7 - 326	101.5	1.4 - 78	20.0	0.33 - 6.40	1.71
Benzo[a]anhracene										
Chrysene										
Chrysene + Triphenylene					8.7 - 74.0	34.0	5.1 - 42.8	17.1	1.60 - 6.10	2.36
Benzo[b]fluoranthene										
Benzo[k]fluoranthene										
Benzofluoranthenes [b+j+k]					5.7 - 44.3	26.4	1.8 - 16.8	5.0	0.26 - 1.30	0.51
Benzo[e]pyrene					6.4 - 48.9	30.6	1.3 - 10.7	3.7	0.23 - 1.10	0.43
Benzo[a]pyrene	8 - 17	12	1.3 - 1.7	1.4	5.2 - 35.1	18.4	0.7 - 11.9	4.0	0.13 - 0.60	0.22
Perylene					1.9 - 10.0	5.1	0.4 - 2.7	0.7	0.11 - 0.35	0.15
Indeno[1,2,3-cd]pyrene					2.1 - 12.5	7.9	0.8 - 9.0	2.5	0.06 - 0.28	0.12
Dibenz[ah]anthracene										
Benzo[ghi]perylene					4.4 - 85.2	48.1	2.1 - 16.0	4.8	0.20 - 0.78	0.33
Anthanthrene					1.6 - 10.8	5.6	0.5 - 4.4	1.3	0.02 - 0.12	0.04
Coronene					2.8 - 29.4	16.6	0.1 - 6.4	1.5	0.02 - 0.13	0.08
Benzo[b]naphtho[2,1-d]thiophene					NA	NA	0.7 - 4.3	2.2	0.78 - 6.20	1.89

ND: not detected

[a] Table 38 ; Data from "composite used automotive oil" combined with data from "used oil feedstock to re-refiner"

[b] Table 2

[c] Table 3

	U.S. EPA (1984)[d]		Pruell & Quinn (1988)[e]		Upshall et al. (1993)[f]	Brinkman & Dickson (1995)[g]		Meinz et al. (2004)[i]	
	Range (ug/g)	Mean (ug/g)	Range (ug/g)	Mean (ug/g)	Mean (ug/g)	Range (ug/mL)	Mean (ug/mL)	Range (ug/g)	Mean (ug/g)
Naphthalene	110 - 1400	475	854 - 2520	1910	52	ND - 1443	196	198 - 1270	677
Acenaphthylene					1.5	ND - 134	2		
Acenaphthene					3.7	ND - 171	7		
Fluorene			42 -109	83	67	ND - 304	21		
Phenanthrene			99 -193	159	200	ND - 1387	81		
Anthracene			25 – 47	34	22	ND - 127	9		
Fluoranthene			70 – 91	78	55	ND - 2826	308		
Pyrene			80 – 96	88	120	ND - 1859	357		
Benzo[a]anhracene	ND - 660	71.3	28 – 47	36	38	ND - 726[h]	65 [h]		
Chrysene			49 – 85	61	45				
Chrysene + Triphenylene									
Benzo[b]fluoranthene						ND - 93	9		
Benzo[k]fluoranthene						ND - 111	6		
Benzofluoranthenes [b+j+k]					46				
Benzo[e]pyrene			ND – 27	11	32				
Benzo[a]pyrene	ND - 405	24.6	ND – 22	9	15	ND - 65	10		
Perylene					1.1				
Indeno[1,2,3-cd]pyrene					14	ND - 77	4		
Dibenz[ah]anthracene					1.5	ND - 94	8		
Benzo[ghi]perylene					72	ND - 193	20		
Anthanthrene									
Coronene									
Benzo[b]naphtho[2,1-d]thiophene									

[d] Table 2 (summary table of data from Tables 15, 16 and 17); n = 25 – 65

[e] Table 2; n = 3 (data are from three different oil changes of the same vehicle running on unleaded gasoline); minimum detection limit (MDL) = 5 ug/g for all PAHs

[f] Table 1; n = 1

[g] Table 5; data summarized from 96 samples; samples were a composed of vehicle crankcase oil (n=24), quick lube oil (n=16), industrial oil (n=25), used oil from truck and rail tankers (n=22) and re-refinery feedstock (n=9); minimum detection limit (MDL) = 1 ug/mL for all PAHs

[h] Range and mean are for benzo[a]anthracene + chrysene

[i] Range and mean of eight samples collected from individual autos + one sample collected from the tank of a commercial oil change business

APPENDIX B-3
Composition of Used Oil
Organic Compounds

	U.S. EPA (1984)[a]		U.S. EPA (1991)[b]		
			Gasoline Engine	Diesel Engine	Storage Tank
	Range (ug/g)	Mean (ug/g)	Range (ug/g)	Range (ug/g)	Range (ug/g)
Aromatic & Alkyl Aromatic					
Benzene	ND - 55,000	961	ND - 13.2	ND	ND - 420
Toluene	ND - 55,000	2,200			
Xylenes (*o*-, *m*- and *p*- isomers)	ND - 139,000	3,386			
Ethylbenzene					
n-Propylbenzene					
Isopropylbenzene					
1,2,4-Trimethylbenzene					
1,3,5-Trimethylbenzene					
n-Butylbenzene					
sec-Butylbenzene					
Chlorinated					
Methylene Chloride					
1,1,1-Trichloroethane	ND - 110,000	2,800	ND - 25	ND	ND - 2100
Tetrachloroethanes (all isomers)			<25	ND	ND
Trichloroethylene	ND - 26,000	1,388	ND	ND	ND
Tetrachloroethylene	ND - 32,000	1,421	ND	ND	ND - 1700
o-Dichlorobenzene					
m-Dichlorobenzene					
p-Dichlorobenzene					
1,2,4-Trichlorobenzene					
Trichlorobenzene (all isomers)					
PCBs	ND - 3,800	109	ND	ND	ND
Chlorofluorocarbons					
Trichlorofluoromethane					
Dichlorodifluoromethane	ND - 2,200	373			
Trichlorotrifluoroethane	ND - 550,000	62,936			

[a] Table 2 (summary table of data from tables 15, 16 and 17); n = 25-753
[b] Table III.C.3A; n = 2-7 (gasoline engine), n = 1-2 (diesel engine), n = 3-6 (storage tank)

	Brinkman & Dickson (1995) [a]		Meinz et al. (2004)[d]	
	Range (ug/g)	Mean (ug/g)	Range (ug/g)	Mean (ug/g)
Aromatic & Alkyl Aromatic				
Benzene			22 -28	54
Toluene			244 – 1200	658
Xylenes (*o*-, *m*- and *p*- isomers)			216 – 1580	722
Ethylbenzene			104 – 971	241
n-Propylbenzene			74 – 194	135
Isopropylbenzene			14 – 39	26
1,2,4-Trimethylbenzene			618 – 1520	998
1,3,5-Trimethylbenzene			163 – 420	266
n-Butylbenzene			39 – 115	86
sec-Butylbenzene			11 – 32	20
Chlorinated				
Methylene Chloride	ND – 12	ND*	ND – 83	10
1,1,1-Trichloroethane	ND – 887	78		
Tetrachloroethanes (all isomers)				
Trichloroethylene	ND – 59	2	ND	ND
Tetrachloroethylene	ND – 881	63	ND	ND
o-Dichlorobenzene	ND – 42	1*	ND	ND
m-Dichlorobenzene	ND – 7	ND*	ND	ND
p-Dichlorobenzene	ND – 14	ND*	ND	ND
1,2,4-Trichlorobenzene	ND – 60	1*		
Trichlorobenzene (all isomers)	ND – 14	Nd*		
PCBs				
Chlorofluorocarbons				
Trichlorofluoromethane	ND – 105	5		
Dichlorodifluoromethane			ND	ND
Trichlorotrifluoroethane	ND - 66	3		

c Table 5; data summarized from 96 samples; samples were a composed of vehicle crankcase oil (n=24), quick lube oil (n=16), industrial oil (n=25), used oil from truck and rail tankers (n=22) and re-refinery feedstock (n=9)

d Range and mean of eight samples collected from individual autos + one sample collected from the tank of a commercial oil change business

* <10% of samples > DL

APPENDIX B-4
Composition of Residual Oil
(No. 6 fuel oil)

	USEPA (1993)[a]		Graziano &	Raymond et al.	Lloyd's
	Average	Range	Daniels (1995)[c]	(1976)[d]	Register (1995)[e]
Trace Elements (u/g)					
Aluminum	3.8	0.3 - 19		ND	
Antimony					ND - 0.3
Arsenic	0.8	0.02 - 2.0			0.27 - 1.0
Barium	1.3	0.3 - 3.4	0.7 - 95	ND	0.04 - 0.39
Beryllium					0.13 - 0.90
Bismuth					ND - 0.1
Boron				ND	
Cadmium	2.3[b]	0.01 - 0.9[b]	0		ND
Calcium				17	
Chromium	1.3	0.1 - 1.7	13 - 14	1	ND - 0.39
Cobalt					0.18 - 0.65
Copper				ND	0.12 - 0.88
Iron	18	2 - 2200		18	12.0 - 13.9
Lead	3.5	0.1 - 8.0	1.7 - 4.1	ND	ND - 0.15
Magnesium	13	0.8 - 760		21	
Manganese				2	
Mercury					ND - 0.04
Molybdenum				ND	ND - 0.58
Nickel			3 - 118	13	28.1 - 44.0
Phosphorus				ND	
Selenium					ND - 0.34
Silicon				ND	
Silver				ND	
Sodium				27	
Strontium					ND - 0.08
Tin				3	ND - 0.3
Titanium					0.12 - 0.23
Tungsten					ND - 0.53
Vanadium	160	1 - 110		38	73.0 - 100.3
Zinc	1.3	0.6 - 35	0	12	0.60 - 0.90
Other					
Ash, wt%	0.25	---	0 - .5		
Total Halogens, ppm			---		
Chlorine, wt%	0.0012	.0003 - .038			
Nitrogen, wt%	0.35	.15 - .5	---		
Sulfur, wt%	1.0	.2 - 2.8	.3 - .4	0.66	

[a] Table 2-1; number of samples not provided. Data apparently based on samples collected and analyzed in 1982-1983. Published in reports by USEPA (1984) and AD Little (1983)

[b] Despite the obvious discrepancy, these data were transcribed correctly

[c] Original data source: Mueller & Associates, Inc. (1989)

[d] Tables 1(sulfur only) and 2 (all other elements); n = 1

[e] Table 17 (n=3); values shown are the ranges of concentrations detected in 3 fuel oil samples

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