

5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Fuel oils are complex mixtures of aliphatic and aromatic hydrocarbons whose exposure potentials are based on the environmental fate of the individual components of the mixtures, particularly n-alkanes, branched alkanes, benzene and alkylbenzenes, naphthalenes, and PAHs.

Fuel oils may enter the water or soil environment as a result of spills during use or transportation or from leaking storage facilities or pipelines. The more volatile components of fuel oils (low molecular weight alkanes) will evaporate from the soil or water and enter the atmosphere where they will be degraded. The higher molecular weight aliphatic components ($>C_{20}$) of fuel oils have very low water solubility and will not volatilize from soils or surface waters. Consequently, these heavier compounds will remain on the soil or in the water column where they may be adsorbed to particulate organic matter in water or soil and, in water, will settle to the sediment. They will eventually be biodegraded by microorganisms in the soils and sediments. The rate and extent of biodegradation are dependent on the ambient temperature, the presence of a sufficient number of microorganisms capable of metabolizing these hydrocarbons, the amount of aromatic species in a given oil, and the concentration of fuel oil. The aromatic components (benzene and alkylbenzenes) of fuel oils tend to partition into the polar phase of the environment and migrate through the soil to the groundwater. However, these components of fuel oil are also the most biodegradable.

The National Occupational Exposure Survey conducted by NIOSH between 1980 and 1983 estimated that 96,345 employees were exposed to fuel oil no. 2, 1,526 workers were exposed to fuel oil no. 4, and 1,076,518 employees (including 96,255 females) were exposed to kerosene in the workplace. Worker exposure was most likely in industries associated with machinery and special trade contractors. General population exposure is potentially the greatest for persons living near an area where fuel oils have been dumped and have migrated into the groundwater or when fuel oil vapor has penetrated the soil and may enter basements of buildings.

Fuel oil no. 1 has been identified in 23 of the 1,397 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL), and fuel oil no. 2 has been identified in at least 4

of the NPL sites (HAZDAT 1991). The frequency of these sites within the United States can be seen in Figures 5-1 and 5-2.

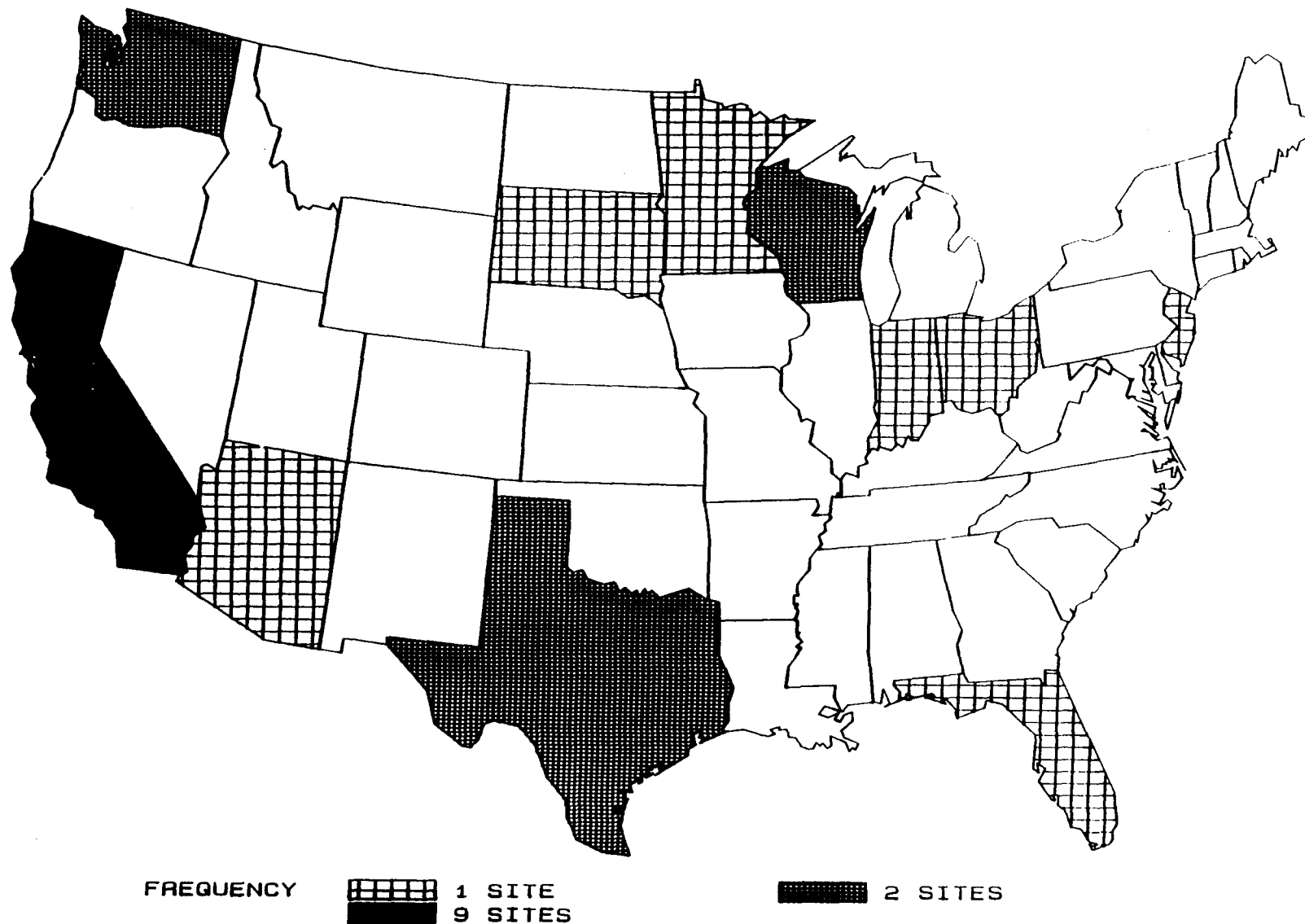
5.2 RELEASES TO THE ENVIRONMENT

Releases of fuel oils are not required to be reported under SARA Section 313; consequently, there are no data for these compounds in the 1990 Toxics Release Inventory (TR190 1992).

5.2.1 Air

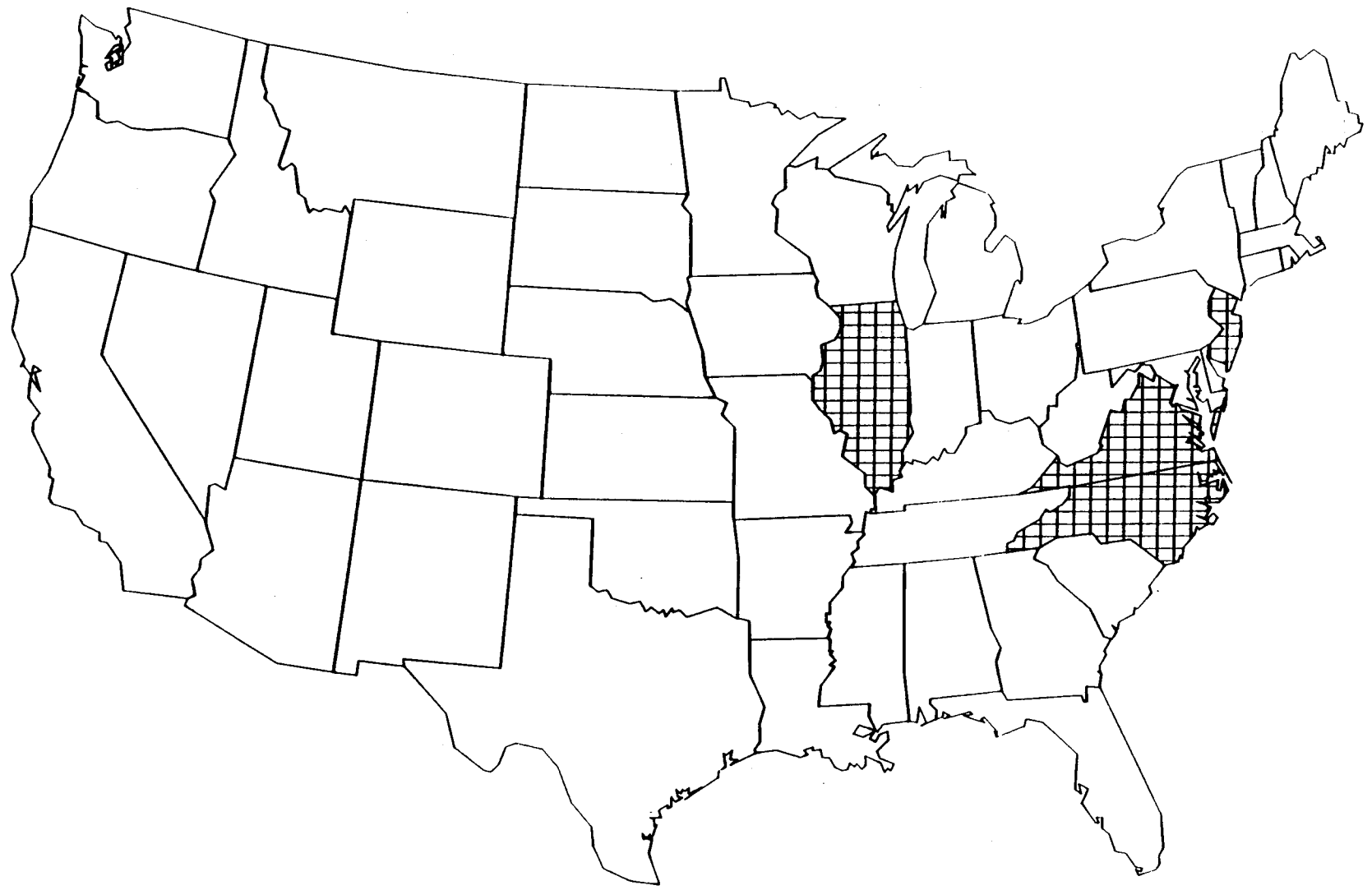
Fuel oils may be released to air as fugitive emissions from storage facilities or as a result of their use as fuel for combustion engines; in stoves, lamps, and furnaces; and as solvents. Atmospheric emissions of a fuel oil may be determined primarily by detection of its volatile hydrocarbon components. Atmospheric releases of fuel oil no. 1 (kerosene) may be expected as a result of its use as a solvent for insecticides and fungicides and by evaporation from open containers when used as a fuel. Indoors, unvented kerosene heaters are a source of sulfur dioxide, nitrogen dioxide, carbon monoxide, respirable suspended particulate matter, and acids in the vapor and particulate phase (Koutrakis et al. 1992; WHO 1991). In mobile homes in particular, use of kerosene heaters resulted in an increase in CO and airborne unburned kerosene fuel, an increase in mutagenicity of particle-phase organics, and little mutagenicity in the semivolatile organics (Mumford et al. 1991). Emission rates of carbon monoxide from unvented kerosene heaters in mobile homes were measured to be 10 to 272 $\mu\text{g}/\text{kJ}$ for convective heaters, and 57 to 264 $\mu\text{g}/\text{kJ}$ for radiant heaters; concentrations of CO averaged 7.4 ppm with a peak of 11.5 ppm. Hydrocarbon emissions detected at fixed-roof fuel oil and low vapor pressure distillate storage tanks were only 8% of the emissions estimated for these facilities using the equations developed by the American Petroleum Institute (Wilson et al. 1978). The relationships have been quantified between the components in diesel fuel blends, the variables of the emissions when the fuel is burned, and their biological effects (Westerholm and Egerback 1991). Combustion from kerosene heaters contributes to the radon progeny particle size distribution in particles in the size range of 0.02-0.08 μm (Tu et al. 1991). Fuel oil combustion was determined to be a negligible contributor to atmospheric aerosol particles in the Toyama Prefecture of Japan (Toriyama et al. 1991). For residential oil furnaces, the mutagenicity of emissions in revertants per megajoule increases as particulate emissions increase, and emissions are up to 3 orders of magnitude


FIGURE 5-1. FREQUENCY OF NPL SITES WITH FUEL OIL NO. 1 CONTAMINATION *



*Derived from HazDat 1994

FIGURE 5-2. FREQUENCY OF NPL SITES WITH FUEL OIL NO. 2 CONTAMINATION *



FREQUENCY  1 SITE

*Derived from HazDat 1994

less mutagenic than wood smoke from conventional, uncontrolled woodstoves on a per unit of fuel energy value (EPA 1992).

Fuel oils are released to the atmosphere as vapor when used as smoke screens or fogs by the U.S. Army; concentrations may range from 13 to 2,000 mg/m³. Deposition of these particles to soil and water may result in fallout concentrations of 6-60 g/m² (Army 1986).

5.2.2 Water

Fuel oils may be released to surface waters as a result of fuel spills from transport vessels or from facilities located adjacent to surface waters, in runoff from industrial facilities where they are used as fuels or solvents, or from the intentional disposal of excess fuel oils down drains. Kerosene may enter surface and groundwater as a result of leaking aboveground and underground storage tanks, including those found at disposal facilities for spent nuclear fuel reprocessing operations (DOE 1989c). In 1988, a rupture of an aboveground storage tank outside of Pittsburgh, Pennsylvania, released more than 1,000,000 gallons of fuel oil no. 2 into the Monongahela and Ohio Rivers and disrupted local drinking water supplies (MacKerron and Kiesche 1988). Fuel oils may enter the marine ecosystem as a result of accidental spills from transport vessels, such as occurred when an oil barge released more than 650,000 liters of fuel oil no. 2 into Buzzards Bay, Massachusetts, in 1969 (EPA 1981); a second spill occurred in this area in 1974 (Bums and Teal 1979; Teal et al. 1978). Since 1915, ships and barges containing fuel or oil have sunk in Puget Sound or adjacent waters. Nine of these vessels have been classified as posing a potential hazard to human health or the aquatic environment because they have not been salvaged and contain large known reservoirs of fuel or oil, some which may have been discharged after sinking (EPA 1991d). Between 1986 and 1991, 4.6 million gallons of fuel oil no. 2 and 12.6 million gallons of fuel oil no. 6 were reported released into Newark Bay, New Jersey (Gunster et al 1993a). A significant source of petroleum to the bay appears to be municipal and industrial wastewater treatment facilities; over 600,000 gallons of petroleum products have been discharged since 1982 (Gunster et al 1993b). Approximately 170,000 gallons of diesel fuel arctic entered the marine ecosystem surrounding Arthur Harbor on the Antarctic Peninsula in 1989 when an Argentine resupply/tourist ship sank (Karl 1992), and in 1988, 230,000 gallons of Bunker C fuel oil was released from a barge off the Washington coast (Strand et al 1992).

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Fuel oils that are accidentally released to inland waters are reported to the Emergency Response Notification System (ERNS). Total spill volumes of fuel oils released in 1991 were as follows (ERNS 1992):

<u>Fuel oil</u>	<u>No. of notifications</u>	<u>Gallons released</u>
No. 1	8	43,190
No. 1-D	20	3,292
No. 2	916	14,558,313
No. 2-D	28	2,769
No. 4	35	12,239

Storm runoff from an industrial site in Rhode Island used by oil distributors, scrap metal dealers, and metal finishers contained a hydrocarbon product resembling fuel oil no. 2. This product comprised 4% of the total petroleum hydrocarbons detected in the runoff, most of which were associated with crankcase oil (Latimer et al. 1990). Two freighters collided off the coast of South Africa in 1992; the freighter transporting 160 tons of marine fuel oil and 53 tons of gas oil sank (Molden 1992).

5.2.3 Soil

Fuel oils may be released to soil as a result of accidental spills (Strayer et al. 1983; Rosenblatt and Montemagno 1992) and leaking from underground storage tanks or pipelines. Hydrocarbon contamination (due to diesel fuel spillage and leakage related to ship and boating activities) has been measured in sediment samples in Arthur Harbor on the Antarctic Peninsula (Kennicutt et al. 1994). Also, approximately 200,000 gallons of liquid hydrocarbons were released into the underlying soil at a fuel-storage terminal in northern Virginia. The soil vapor above the resultant hydrocarbon plume and the groundwater below were analyzed for total and individual petroleum hydrocarbons (Mushrush et al. 1994).

5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

The transport and dispersion of fuel oils are dependent on the water solubility and volatility of the aliphatic and aromatic hydrocarbon fractions. Lower molecular weight hydrocarbons such as *n*-alkanes may volatilize relatively quickly from both water and soil, while larger aliphatics (greater than C₉ chain length) may be sorbed to organic particles in water or soil. Aromatic hydrocarbons will be dissolved in the aqueous phase in both soil and water and may undergo some volatilization.

Aerosol oil particles of SGF-1, a distillate oil chemically similar to fuel oil no. 2, used by the military to generate oil fogs (particle diameter of 0.5-1.2 μm) may remain aloft for approximately 1 hour, may be transported 1-10 km (average of 5 km) downwind during this time, and, with the exception of evaporative losses, will be deposited to soil or surface waters (Army 1986; Liss-Suter et al. 1978).

The solubility of fuel oil no. 2, particularly the alkane and isoprenoid fractions, in seawater is increased by the presence of fulvic acid, although the solubilities of phenanthrene or anthracene, both polycyclic aromatic hydrocarbons, are unaffected by the presence of humic materials (Boehm and Quinn 1973). Unfiltered Narragansett Bay water was able to dissolve 1,560 μg/L of fuel oil no. 2, although removal of dissolved organic material from the water reduced the solubility by 33-60% (Boehm and Quinn 1974). The water-dissolved fraction of JP-5 fuel was stable for 24 days (Edgerton et al. 1987).

The microlayer at the air-water interface may be composed of different fuel oil hydrocarbons than the subsurface waters. When fuel oil no. 2 was added below the surface of a marine ecosystem, the microlayer was enriched for both saturated and aromatic hydrocarbons compared with the subsurface water, with a significantly greater proportion of total saturates compared with aromatics. The hydrocarbons in the microlayer were predominantly higher molecular weight hydrocarbons, greater than C₁₈ for saturates and phenanthrene (F₂) for aromatics. This indicates that there is transport of all the hydrocarbons from the water column to the microlayer and weathering of the hydrocarbons by evaporation once in the microlayer (Gearing and Gearing 1982b). Weathering of fuel oil spills on water surfaces is dependent on the vapor pressures of the hydrocarbon components and can be correlated with the evaporation rates of the alkanes present in the fuel oil mixture. Components with

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vapor pressures higher than n-octane rapidly evaporate from the surface of the fuel oil spill while those with vapor pressures lower than n-octadecane persist and may result in a more viscous residue, eventually retarding the evaporation of other components (Regnier and Scott 1975).

Addition of fuel oil no. 2 to a laboratory marine ecosystem showed that the insoluble, saturated hydrocarbons in the oil were slowly transported to the sediment on suspended particulate material. The particulate material contained 40-50% of the total amount of aliphatics added to the system and only 3-21% of the aromatic fraction (Oviatt et al. 1982). This indicates that most aromatic hydrocarbons are dissolved in the water (Coleman et al. 1984), whereas the aliphatic hydrocarbons are not (Gearing et al, 1980; Oviatt et al. 1982). In a similar experiment, when fuel oil no. 2 was added continuously to a marine ecosystem for 24 weeks, oil concentrations in the sediment remained low until 135 days after the additions began, but then increased dramatically to levels that were 9% of the total fuel oil added (108 g/tank) and 12% of the total fuel oil saturated hydrocarbons. The fuel oil concentrations in the sediment began to decrease quite rapidly after the maximum levels were reached. The highest sediment concentrations of saturated hydrocarbons (106-527 $\mu\text{g/g}$) were found in the surface flocculent layer, with concentrations decreasing with sediment depth from 22 $\mu\text{g/g}$ to not detectable at 2-3 cm below the sediment surface. Fuel oil was being transported to the sediments adsorbed to suspended material in the water column with smaller particles (<45 μm) containing 2.2 times more fuel oil than larger particles (>45 μm) (Wade and Quinn 1980). Although biodegradation may remove many of the soluble, aromatic hydrocarbons, a residue of 10-20% of the total added oil, composed primarily of branched alkanes, cycloalkanes, and aromatics, may remain in the top 2 cm of the sediment for over a year (Gearing et al. 1980; Oviatt et al. 1982). A spill of fuel oil no. 2 to waters off Massachusetts showed that the oil was detected at distant monitoring locations 46 months after the spill, although the concentration in the sediments remained the greatest in the vicinity of the original spill. Oil continued to move in pulses from more polluted areas to less polluted areas for several years after the spill, with much of the oil being exhumed from sediments in the shallower waters as a result of storm action (EPA 1981). Movement of the oil to adjacent salt marshes indicated that the oil was sorbed to the anoxic sediments where it persisted (Bums and Teal 1979).

The partitioning of fuel oil no. 2 and kerosene into drinking water after 17 hours of incubation resulted in only 1.0% of the fuel oil and 0.7% of the kerosene being dissolved in the water. Further analysis of these fuels indicated that although each compound contains approximately 50% aliphatic

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hydrocarbons (by weight percent), the water-soluble fractions contained primarily aromatic constituents (>93%) including benzenes and naphthalenes as shown below (Coleman et al. 1984):

	<u>Water-soluble fraction</u>		
	<u>Whole product*</u>	<u>1/2 hour</u>	<u>17 hours</u>
<u>Kerosene</u>			
Alkanes + cycloalkanes	68.6	4.5	0.5
Benzene + substituted benzenes	13.7	63.5	53.2
Naphthalene + substituted naphthalenes	5.7	29.6	44.8
<u>Fuel oil no. 2</u>			
Alkanes + cycloalkanes	48.0	<0.5	<0.5
Benzene + substituted benzenes	4.5	25.8	19.4
Naphthalene + substituted naphthalenes	32.4	73.4	79.7

*Estimated weight percent

Partitioning of eight PAHs between four diesel fuels and water can be described using Raoult's law for activity coefficients (Lee et al. 1992).

A coal-liquid spill resulted in soil penetration to a depth of 8 meters; the soil was described as crushed stone mixed with glacial outwash sand and gravel. Soil columns collected 6 months after the spill were leached with a synthetic rain solution, and the leachates were collected and analyzed for total phenolics. Over the 12-month leaching period, the phenol fraction of the residual coal-derived fuel decreased by 98%, primarily by dissolution. Groundwater monitoring down-gradient from the spill detected phenols even though the surface of the spill had been sealed to prevent leaching of water-soluble components by precipitation (Strayer et al. 1983).

The movement of a synthetic kerosene through soil was found to be dependent on the moisture content of the soil. The greater the moisture content (i.e., 4% compared with 0.8%) of the soil, the less the adsorption of the more volatile components of the kerosene and the greater and the more rapid the penetration of the liquid component through the soil. Conversely, the upward mobility of both the liquid and vapor phases of kerosene through soil decreased with increased moisture content, and at field capacity, the upward capillary movement of the kerosene was completely inhibited (Acher et al.

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1989). Desorption of a simulated kerosene applied to three types of soil, each with a moisture content at 70% of field capacity, was found to be complete after 30 days of exposure to the atmosphere with the slowest desorption from the soil having the greatest organic content (Yaron et al. 1989). Kerosene loss from a dune sand, a loamy sand, and a silty loam soil after 50 days showed that volatilization of all kerosene components was greatest from the dune sand and loamy sand soils. The larger pore size of these types of soil compared with the silty loam soil was thought to be the reason for the increased volatilization (Galín et al. 1990a). Movement of kerosene through three grades of sand was affected mainly by volatilization of the C₉—C₁₃ components with a subsequent increase in the viscosity of the remaining kerosene residue and a decrease in the infiltration rate through the inert porous media (Galín et al. 1990b).

The movement of kerosene through various types of soil over a 12 hour period was studied. Upward, downward, and lateral movement was greatest in soil of the mica/kaolinite type (11% clay content) 40, 102, and 45 cm, respectively. Movement through soils that were primarily kaolinite (clay content of 26-52%), regardless of the direction, ranged between 20 and 33 cm (EPA 1986b). Application of herbicides such as *S*-ethyl dibutylthiocarbamate to a field using kerosene or fuel oil no. 2 as solvents (up to a volume of 40 gallons per acre) increased the inactivation of the herbicide on soil, whereas acetone, benzene, or xylene did not. The accelerated inactivation possibly resulted from a change in surface tension that facilitated the volatilization of the herbicide from the soil (Danielson and Gentner 1970).

Studies on the permeability of compacted micaceous soil used as a potential liner for landfills found that the permeability of the soil to kerosene and diesel fuel was 3-4 orders of magnitude greater for kerosene and 1-1.5 orders greater for diesel fuel compared with water (EPA 1984).

Aquatic organisms are known to bioconcentrate hydrocarbons. Addition of fuel oil no. 2 (containing 38% aromatics) to a commercial shrimp pond gave an initial concentration of approximately 0.03 ppm for total naphthalenes. The concentration of total naphthalenes (toxic components of fuel oil) peaked at approximately 0.3 ppm in the water after 48 hours and slowly decreased to background levels after 38 days. Sediment concentrations of the total naphthalenes rose from 0 ppm at 6 hours after the application of the fuel oil to 2 ppm at day 1, peaked at 14 days (9 ppm), and slowly declined to 1.5 ppm at 296 days. The concentrations of total naphthalenes in shrimp, clams, and oysters peaked at 24, 48, and 72 hours, respectively, with maximum concentrations in each organism exceeding the

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naphthalene concentrations in the ambient water. When the contaminated organisms were placed in clean water after 38 days of exposure in the shrimp pond, depuration (to background levels) was complete after 10 days for shrimp and after 47 days for oysters, indicating that the concentrations in marine organisms are more closely correlated with water concentrations than with sediment concentrations of aromatic hydrocarbons (Cox et al. 1975). Lobsters exposed to a pulse of fuel oil no. 2, which simulated a small spill, were found to bioconcentrate PAHs (components of the fuel oil) in the hepatopancreas and muscle tissue within 34 days after exposure. PAH levels continued to be elevated at days 10 and 11; however, depuration to control levels occurred by day 20-21 (Williams et al. 1989, 1991).

Mussels (*Mytilis edulis*) exposed to a small spill (approximately 6,000 liters) of fuel oil no. 2 were followed for 86 days post-spill to assess the uptake and retention of the fuel oil components. Alkanes, cycloalkanes, and aromatic concentrations increased significantly in the mussel tissue the 1st day; however, by day 5 post-spill, the *n*-alkanes were barely detectable, and by day 21, the concentration of the unresolved complex mixture of alkanes-cycloalkanes was 30% of the day 1 concentrations. Concentrations of lower molecular weight aromatics (e.g., naphthalenes) decreased before the higher molecular weight aromatics (e.g., phenanthrenes). The biological half-lives of some fuel oil no. 2 components in mussels were as follows: *n*-C₁₆--0.2 days; *n*-C₂₃--0.8 days; C-2 naphthalene--0.9 days; C-3 naphthalene--1.5 days; phenanthrene--2.1 days; and unresolved complex mixture--2.8-3.9 days (Farrington et al. 1982a). Similar results were found in sea scallops (*Aequipecten irradians*), which showed a gradual depletion of straight chain and branched chain hydrocarbons after exposure to fuel oil no. 2. However, the more toxic aromatic hydrocarbons were retained in scallop tissue for several months after exposure (Blumer et al. 1970). Sea mullet exposed to 5 ppm kerosene in sea water had a kerosene-like taint after 24 hours of exposure. In another study, oysters exposed to fuel oil no. 2 at 400 ppm for 8 hours accumulated 312 ppm of PAHs and 8.7-21.8 ppm of naphthalenes in their tissues; however, over 90% of the *n*-paraffins were released within 24 hours when the oysters were returned to oil-free water. Depuration of the aromatic hydrocarbons was much slower. When shrimp, clams, and fish were exposed to the water-soluble fraction of fuel oil no. 2, shrimp rapidly accumulated total naphthalenes for an hour then released them, clams accumulated the naphthalenes at a slower but constant rate for 24 hours, and the fish accumulated the naphthalenes very rapidly during 2 hours of exposure; all three species rapidly released the accumulated naphthalenes when placed in oil-free water with low or undetectable levels at 14 days (Anderson and Neff 1977).

5.3.2 Transformation and Degradation

The fate of four petroleum mixtures has been evaluated using three approaches—evaluating the fate of (1) indicator chemicals, (2) the mixture of the whole with a surrogate, and (3) the hydrocarbon mixture as a whole. The four mixtures were crude oil, JP-5, mineral spirits, and diesel. The choice of approach requires the consideration of availability and quality of data on the mixture, the mobility and toxicity of the mixture, and the availability of site data (Custance et al. 1992).

5.3.2.1 Air

No studies on the transformation or degradation of fuel oils in the atmosphere were located. However, volatile components of fuel oils such as benzene, toluene, xylenes, and PAHs may be expected to enter the atmosphere where they are subjected to degradation processes. Further information on the atmospheric degradation of selected volatile hydrocarbons are presented in the ATSDR toxicological profiles for these chemicals (ATSDR 1989, 1990a, 1991a, 1991b).

5.3.2.2 Water

The photooxidation of fuel oil no. 2 in water is quite rapid in sunlight. The rate is four times that of coal liquids, producing two photooxidant pools with reaction rate constants of 0.58/minute and 0.037/minute. The faster reacting photooxidant was tentatively identified as hydrogen peroxide and the slower reacting pool as a mixture of indane and tetralin hydroperoxides (Herbes and Whitley 1983). Two mechanisms appear to result in the formation of the peroxides: (1) reaction of free radicals with triplet oxygen to produce peroxy radicals and hydroperoxides, which in turn continue the chain reaction; and (2) formation of hydroperoxides by direct addition of excited singlet oxygen to reactive acceptors in the oil such as olefins. These reactions reached a maximum after approximately 90 hours of irradiation. Other photodegradation products of fuel oil exposed to ultraviolet radiation include phenols (linear increase in concentration during 165 hours of irradiation), naphthols, and carboxylic acids (Larson et al. 1977, 1979).

Biodegradation of fuel oils is dependent on the degradation of the various hydrocarbon fractions present in the oils. The relative order for biodegradation of the hydrocarbon fractions from the most readily degraded to the least is as follows: *n*-alkanes, iso-alkanes, olefins, low molecular weight

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aromatics (at low, non-toxic concentrations), PAHs, and cycloalkanes (Bartha and Atlas 1977; Edgerton et al. 1987).

Water and sediment samples taken from Muddy Creek in the Rhode River of Chesapeake Bay were inoculated with 0.1% (volume/volume) of fuel oil no. 2 and incubated for 28 days. Growth of aerobic bacteria and fungi was enhanced by the addition of the fuel oil, although growth of yeast was inhibited (Walker and Colwell 1975). A mixed culture of estuarine bacteria was observed to degrade fuel oil no. 2 by 55% in 28 days with the primary microorganisms being *Bacillus* and *Pseudomonas*. Degradation of aromatic components was significantly greater than the n-alkanes (Walker et al. 1976).

Microorganisms readily able to degrade hydrocarbons were found in the Neuse River estuary in North Carolina. Although the estuary was relatively free of hydrocarbon contamination, 63% of the bacteria and 71% of the fungi isolated from surface water samples were able to utilize kerosene as the sole carbon source (Buckley et al. 1976). Weathered kerosene (volatile components were allowed to escape prior to testing) was spiked with four marker hydrocarbons, and the degradation of the markers was monitored. All four markers were degraded by a water-sediment mixture from an "oiled arm" of an Ohio lake; more rapid degradation was associated with mixtures taken from relatively polluted areas of the lake (Cooney et al. 1985), suggesting that biodegradation is enhanced by the presence of acclimated microorganisms. Marine bacteria capable of using fuel oil nos. 1, 2, and 4 were isolated from Narragansett Bay, Rhode Island. Most of the bacteria were found to utilize the aliphatic components of the fuel oils, primarily hexadecane, while only a few of the bacteria were able to degrade the aromatic components. The bacteria were able to degrade the hexadecane at 0°C but degradation was significantly improved when the incubation temperature was increased to 8°C and 16°C; similar but not such dramatic effects were seen in the degradation of naphthalene with increased temperature (Cundell and Traxler 1976).

The degradation of hydrocarbons fractions of fuel oil no. 2 was studied using a marine microcosm under different temperature, light, and biological activity regimes. Initial fuel oil concentrations ranging from 151 to 189 µg/L were found to decrease exponentially under all regimes, with temperature having the greatest effect on the half-lives of the component hydrocarbons. In cold water (0-2 °C), the half-life for total hydrocarbons was greater than 10 days, while in warmer water (17-21°C) the half-life decreased to approximately 30 hours. In cold water, saturated hydrocarbons were removed more rapidly than aromatic hydrocarbons, but in warmer water the half-lives of the

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fractions were similar. For the saturated hydrocarbons, the half-life increased with increasing molecular weight or with branched or cyclic moieties, i.e., small *n*-alkanes (C-12) had the shortest half-life in both warm and cold water. Poisoning the microcosm to eliminate biodegradation had no effect on the degradation of saturated hydrocarbons other than *n*-alkanes, but decreased the rate of aromatic degradation by half, indicating that biodegradation is a significant removal process for both *n*-alkanes and aromatics. Saturated hydrocarbons other than *n*-alkanes are most likely to be removed by adsorption to particulate material in the water followed by sedimentation or the formation of a micelle, which may rise to the surface of the water and evaporate. In cold water, aromatics are most likely to be removed by volatilization, whereas in warmer water, biodegradation is the more important removal process. Photooxidation did not appear to be a significant removal process for either hydrocarbon fraction (Gearing and Gearing 1982a).

Fuel oil no. 2 (average water column concentration 182 µg/L) was added to the Marine Ecosystems Research Laboratory (MERL) system for 5.5 months with a 2-month recovery period. Hydrocarbon concentrations were then measured in the sediment and benthic organisms (*Glyceru americana*, a carnivorous polychaete, and *Crepidulu sp.*, the common slipper shell). The alkane-cycloalkane and aromatic fractions in the benthic organisms were suggestive of partially degraded fuel oil no. 2, and for the aromatic hydrocarbons, were at least an order of magnitude greater than in the control tank. Phenanthrenes, although present at lower concentrations in fuel oil no. 2 than naphthalenes, were present at greater concentrations in the benthic organisms, suggesting that there is a bioaccumulation potential for these compounds. Organism-specific differences show that organisms in close contact with the sediment had relatively higher concentrations of lower molecular weight naphthalenes, as these compounds are more readily retained in the sediment than the water column. Similarly, organisms that live in the water column contained fewer naphthalenes. These results indicate that fuel oil no. 2 degradation products are taken up by benthic organisms, that they may be selectively retained in both sediments and aquatic organisms, and may thus enter the food chain (Farrington et al. 1982b). After 3 months of exposure in a marine intertidal zone, the concentration of fuel oil no. 2 in the mean lower low water (MLLW) area and 2 feet above the MLLW area had decreased by 30% and 53%, respectively (NOAA 1982). Straight-chain alkanes degrade more readily than branched alkanes with a ratio of 1.67 (*n*-C₁₇/pristine), although this ratio will decrease as biodegradation of the *n*-alkanes progresses (Blumer et al. 1970; EPA 1981). Following spills of fuel oil no. 2 into Buzzards Bay, Massachusetts, the concentrations of aromatic hydrocarbons decreased by a factor of 5 within 6 months of the spills with lighter molecular weight compounds decreasing at a faster rate than the

heavier molecular weight compounds. Aromatics such as naphthalenes and phenanthrenes were still present in the marsh sediments at concentrations above background, 6.5 years after the spills (Teal et al. 1978). The oil was sorbed to the anoxic marsh sediments, although biodegradation and dissipation resulted in the decrease of *n*- and branched alkanes from the surface sediment within 4 years. Even 8 years after the spill, some sediments contained over 1,200 ppm petroleum hydrocarbons, with naphthalene and heavier aromatics expected to persist for many more years (Burns and Teal 1979). Twenty years after the spill, some sediments contained trace amounts of biodegraded fuel oil (Teal et al. 1992).

Petroleum residues were measured in the northern Arabian Sea to assess the contamination following the oil spills resulting from the Gulf War in 1991. Little change in variables related to oil pollution took place in any compartment of the marine environment-water, plankton, fish, and sediments (Sengupta et al. 1993).

Groundwater contamination by fuel oil no. 2 and gasoline was detected in wells of a residential area of Rhode Island. While the total hydrocarbon content of the groundwater samples taken at one particular well decreased from 2,350 to 1,580 µg/L over a 19-month period and the percentage of hydrocarbons associated with gasoline also decreased from 58% to 22%, the percentage of hydrocarbons attributable to fuel oil no. 2 increased from 42% to 78%. These data indicate that the gasoline hydrocarbons are more readily removed compared with the higher molecular weight hydrocarbons from fuel oils (Zheng and Quinn 1988).

5.3.2.3 Soil

Microbial degradation in soils is greatest for the aromatic fractions of fuel oils, while the biodegradation of the aliphatic hydrocarbons decreases with increasing carbon chain length. Evaporation is the primary fate process for these aliphatics (Air Force 1989).

A single application of approximately 21, 14, or 13 g/kg soil of home heating oil no. 2 to outdoor plots in Pennsylvania (silt loam), Oklahoma (sandy loam), and Texas (clay loam) was degraded by 86%, 90%, and 86%, respectively, after 1 year, with degradation being independent of temperature differences. Very little oil was present in runoff and leachate water from the sites; however, analysis of ether-extractable compounds in the leachate at the plots suggested that incomplete degradation of

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some individual components in the oils was taking place. Of the six oils tested, no. 2 home heating oil resulted in the largest increase in the number of hydrocarbon-utilizing microorganisms in the plots, and it was the most lethal to soil nematodes (Raymond et al. 1975, 1976). The degradation of kerosene in soil was further studied when a pipeline ruptured and showered a wheat field with kerosene. After 6 months, the kerosene concentration began to decrease in the upper 30 cm of soil (with C13-C17 *n*-alkanes disappearing more rapidly compared with C10-C12 *n*-alkanes) and at 21 months was reduced to trace amounts; however, kerosene was still detected at soil depths of 30-45 +cm. The authors interpreted this as indicating reduced aerobic biodegradation at this depth, especially since the compounds disappeared in the order of their preferential microbial utilization. Seed germination studies using the contaminated soil 1 year after the spill (0.34% kerosene concentrations) showed that kerosene delayed seed germination but that the percent germination was unaffected (Dibble and Bartha 1979). Landfarming techniques (tillage of soil using agricultural implements), developed in the Netherlands to enhance biodegradation of contaminants, demonstrated that after one growing season, kerosene (initial concentration of 1,000-10,000 mg/kg dry matter) was significantly degraded (final concentration of 500 mg/kg dry matter) in 40 cm of soil (Soczo and Staps 1988).

Application of diesel oil or fuel oil (type unspecified) to soil at 1% or 10% showed that, based on carbon dioxide evolution, degradation did occur. After 12 weeks, the applications of 1% diesel oil and fuel oil were degraded by 45% and 23%, respectively, whereas the 10% applications showed that only 10% of each oil was degraded in this time. Carbon dioxide evolution did not increase with increasing time, indicating that microbial populations were not increasing (Flowers et al. 1984). Addition of nitrogen (as urea) to the soil increases the biodegradation potential of diesel oil and kerosene; however, both oils were found to inhibit the urease activity of soil microbes by up to 47% and 35%, respectively, suggesting that sources of nitrogen other than urea should be used (Frankenberger 1988).

The bacterial species in the genera *Achromobacter*, *Pseudomonas*, and *Alcaligenes*, isolated from the soil of an active oil field in Louisiana, were able to aerobically degrade kerosene as determined by oxygen uptake (Cooper and Hedrick 1976). Soil *Pseudomonas* were able to degrade kerosene to a greater extent than were *Enterobacter* with stationary phases occurring after 10 days and 8 days, respectively (Butt et al. 1988). Seven years after the dumping of sludge containing kerosene at two sites, vegetation at each site showed little recovery. Although the bacterial biomass had declined at

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both sites, microbial activity, as determined by carbon dioxide evolution, was greater at the site that had received more precipitation and had the more aerated soil (Jones 1977).

Oxidation of kerosene (fuel oil no. 1) and diesel fuel (fuel oil no. 2) by soil microbes, as determined by dehydrogenase activity, increased with increasing loading rates for both fuel oils (up to 60% w/w oil/dry soil) for up to 7 days of incubation but decreased thereafter. Dehydrogenase activity in soil treated with diesel fuel was almost twice that of soils treated with kerosene (56 and 32 pg formazan/g soil/24 hours, respectively) (Frankenberger and Johanson 1982).

Biodegradation of fuel oils in sediments is inhibited under anaerobic conditions (Bartha and Atlas 1977). Under anaerobic conditions, some soil microorganisms are capable of nitrate reduction using fuel oils as the carbon source, although nitrite may be an unwanted by-product. However, the addition of a small amount of oxygen (0.2 volume percent oxygen) to the medium can accelerate the degradation of the oil without the concomitant production of nitrite (Riss and Schweisfurth 1987). Thirteen months after the spill in 1988 of 230,000 gallons of Bunker C fuel oil off the Washington coast, only trace levels of oil were found in surface sediments (Strand et al. 1992).

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

5.4.1 Air

No data were located on concentrations of fuel oils in workplace or ambient air.

5.4.2 Water

Analysis of drinking water from Cincinnati, Ohio, in February of 1980, showed the presence of numerous hydrocarbons associated with petroleum products at concentrations ranging from 5 ng/L, for naphthalene to 843 ng/L for benzene (Coleman et al. 1984).

Kerosene was detected at monitoring wells (concentrations were not reported) located at the perimeter of a spent nuclear fuel processing plant in western New York State in 1983. The kerosene had been used as an extractant during plant operations from 1966 to 1972 (DOE 1989c).

Groundwater samples taken from monitoring wells at gasoline stations undergoing remediation in Florida contained both kerosene and fuel oil at unspecified concentrations (Thomas and Delfino 1991a).

Fuel oil no. 2 was detected along with gasoline in groundwater wells in Tiverton, Rhode Island. Over a 19-month period, total hydrocarbon concentrations in the water from one well decreased from 2,350 to 1,580 $\mu\text{g/L}$ during which time the proportion of hydrocarbons associated with fuel oil increased from 42% (987 $\mu\text{g/L}$) to 78% (1,232 $\mu\text{g/L}$), probably as a result of the more rapid degradation of the gasoline (Zheng and Quinn 1988).

Kerosene was detected in a whole water sample from monitoring wells for municipal intakes in California in the $\mu\text{g/L}$ range (STORET 1992).

Background concentrations of total hydrocarbons in Narragansett Bay, Rhode Island, ranged from 0.7 to 4.0 $\mu\text{g/L}$ (Gearing and Gearing 1982a).

5.4.3 Soil

No data were located on levels of fuel oils detected in soils.

5.4.4 Other Environmental Media

Shellfish taken from unpolluted waters have been found to contain between 1 and 12 $\mu\text{g/g}$ wet weight of total hydrocarbons while fish have been found to contain between 4 and 14 $\mu\text{g/g}$ total hydrocarbons (steam distillables) (Connell and Miller 1980). Following a spill of fuel oil no. 2 in the Cape Cod Canal in Massachusetts, edible mussels (*Mytilus edulis*) contained average concentrations of various hydrocarbons up to 4.69 $\mu\text{g/g}$ dry weight on day 1 of the spill; background hydrocarbon levels in the controls did not exceed 0.29 $\mu\text{g/g}$ (Farrington et al. 1982a). Limpets in close proximity to onshore accumulations of hydrocarbon contaminants caused by diesel fuel spillage and leakage related to ship and boating activities in Arthur Harbor on the Antarctic Peninsula have incorporated PAHs into their tissues (Kennicutt et al. 1992b). However, 2 years after the release of 150,000 gallons of diesel fuel in the harbor, little spill-related contamination could be detected in intertidal limpets (Kennicutt and Sweet 1992).

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No data were located that discussed concentrations of fuel oils in other environmental media such as food or terrestrial plants and animals.

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

The National Occupational Exposure Survey, conducted by NIOSH between 1980 and 1983, estimated that 96,345 employees (including 590 females) were exposed to fuel oil no. 2, 1,526 employees were exposed to fuel oil no. 4 and 1,076,518 employees were exposed to kerosene in the workplace (NOES 1992). Most exposure to fuel oil no. 2 was in the electric, gas, and sanitary services industries; exposure to fuel oil no. 4 was greatest in the primary metal industries, and exposure to kerosene was greatest for machinists.

Exposure of the general population to fuel oils is most likely to occur as a result of the use of kerosene and other fuel oils in heaters, furnaces, and combustion engines. Spills of number 2 fuel oil in residential basements can pose a significant health risk; a spill of 21 gallons would present a risk for 8 days or longer (Kaplan et al. 1993). Unintentional exposure to fuel oils may occur as a result of groundwater contamination from spilled fuel oils or contact with soils that have been contaminated with fuel oils.

5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

The extent of potential high exposures to various segments of the population appears to be largely unknown. Workers in the petroleum industry may receive intermittent skin exposure to kerosene and other fuel oils during the refining process. Exposure is most likely to occur during the distillation of crude oil, when monitoring and servicing of equipment are carried out, or when sampling must be done (Runion 1988).

The use of kerosene as a solvent in paints and insecticides increases the likelihood of exposure by painters, particularly when spray applicators are used (Fidler et al. 1987), and in exterminators. Use of a respirator, alternate application methods (brush or roller), and increased ventilation can all reduce worker exposure to the solvent vapor.

Workers in a ball-bearing manufacturing plant in Taiwan had severe dermatitis as a result of exposure to kerosene that was used as a degreasing agent. Eczema and erythema were also prevalent among the workers (Jee et al. 1985).

5.7 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of fuel oils is available. Where adequate information is not available, ATSDR, in conjunction with NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of fuel oils.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that, if met, would reduce or eliminate the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda may be proposed.

5.7.1 Identification of Data Needs

Physical and Chemical Properties The physical and chemical properties of some fuel oils and their primary component chemicals, specifically kerosene and fuel oil no. 2, are well defined and can be used to estimate the fate of these fuel oils following release to the environment (Air Force 1989; IARC 1989). However, the physical and chemical properties of other fuel oils such as no. 1-D, no. 2-D, and no. 4, are not well defined, and data should be gathered in order to estimate the fate of these oils in the environment. Data needs associated with specific compounds that are components of fuel oils (e.g., benzene, toluene, xylene, and PAHs) are presented in the ATSDR toxicological profiles for these chemicals (ATSDR 1989, 1990a, 1991a, 1991b).

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Production, Import/Export, Use, and Release and Disposal. Fuel oils are used primarily as heating oils and in engines (Air Force 1989). Most releases of fuel oils are the result of spills either on land or water (EPA 1981; Strayer et al. 1983). Few data are available on current production volumes for specific fuel oils such as fuel oil no. 4. Further information on the production volumes for each fuel oil, environmental releases, and disposal of fuel oils would aid in assessing the potential for human exposure as a result of accidental or intentional release.

Environmental Fate. The environmental fate of fuel oils is based on the environmental partitioning of the major hydrocarbon fractions. For aliphatic hydrocarbons, volatilization of lower molecular weight alkanes and sorption to organic matter for larger aliphatics, followed by photooxidation and biodegradation, respectively, are the primary degradation processes (Gearing et al. 1980; Oviatt et al. 1982). Aromatic components are most susceptible to biodegradation in warm water or soil, although some volatilization may occur in colder waters (Walker et al. 1976; Gearing and Gearing 1982a). Aromatics, however, are also water soluble and therefore are the most likely fuel oil components to leach through soil into groundwater (Strayer et al. 1983). Aliphatics that sediment out of the water column may persist for over a year (Oviatt et al. 1982). Photooxidation may also be a significant degradation process for fuel oils in surface waters (Larson et al. 1977, 1979). The movement and persistence of fuel oils in water and soils is well studied. Further data on the atmospheric reactions of fuel oils would be helpful in determining the transport of fuel oils through air.

Bioavailability from Environmental Media. The extent of absorption of fuel oils by inhalation, oral, and/or dermal routes is unknown. However, toxicity data are available for humans exposed to various fuel oils by each of these routes (Porter 1990; Reidenberg et al. 1964; Subcommittee on Accidental Poisoning 1962). These data indicate that absorption does occur. The extent of absorption by these routes depends on the volatility, solubility, lipophilicity, and other properties of the specific fuel oil components. Several of these component compounds have been discussed in their individual ATSDR toxicological profiles (e.g., benzene, toluene, xylene, PAHs, and lead), which should be consulted for further information (ATSDR 1989, 1990a, 1990b, 1991a, 1991b). More data linking exposure levels of fuel oils with biological levels of component chemicals would be useful in determining which chemicals in the mixture are most likely to be absorbed and by which routes. This information would aid in determining daily human exposure levels and more accurately assessing the risk associated with exposure to fuel oils.

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Food Chain Bioaccumulation. Studies of the accidental and intentional release of fuel oils to the aquatic environment indicate that aquatic organisms are able to bioaccumulate some hydrocarbon fractions, particularly PAHs (Farrington et al. 1982b); however, depuration does occur if the source of the contamination is removed (Cox et al. 1975; Williams et al. 1989). Further studies are needed to determine the biomagnification potential of the hydrocarbon components of fuel oils, particularly PAHs, up the food chain within aquatic and terrestrial ecosystems. Specific research needs are presented in the individual ATSDR toxicological profiles on specific hydrocarbon components such as benzene, toluene, total xylenes, and polycyclic aromatic hydrocarbons (ATSDR 1989, 1990a, 1991a, 1991b). Research on the biomagnification of fuel oils as actual mixtures would not be useful because they are not available to the food chain as mixtures.

Exposure Levels in Environmental Media. There is limited information available on the levels of fuel oils found in soil or water where fuel oils are used or stored. Most monitoring studies have been conducted in the aquatic environment following an accidental spill (EPA 1981; Teal et al. 1978). More data on levels of fuel oils or their components in the air, water, and soil around facilities where fuel oils are produced, stored, and used would be useful. Data on levels in contaminated surface water, groundwater, and soil are needed to assess the potential risk from these likely sources of exposure.

Exposure Levels in Humans. Workers who use fuel oils in manufacturing and those involved in their transfer may experience increased dermal and inhalation exposures. Workers in the petroleum refining industry, particularly those involved with monitoring and servicing unit equipment, including fuel oil storage tanks, are known to have increased exposure to fuel oils such as kerosene (Runion 1988). Further information is needed to assess the approximate levels of exposure for these populations.

Exposure Registries. No exposure registries for fuel oils were located. These substances are not currently compounds for which a subregistry has been established in the National Exposure Registry. These substances will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to the exposure to these substances.

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A registry does exist for benzene, a component of fuel oils. More information on the benzene exposure registry can be found in the ATSDR toxicological profile for benzene (ATSDR 1989).

5.7.2 On-going Studies

No on-going studies on the exposure or environmental fate of fuel oils were located.

