

5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

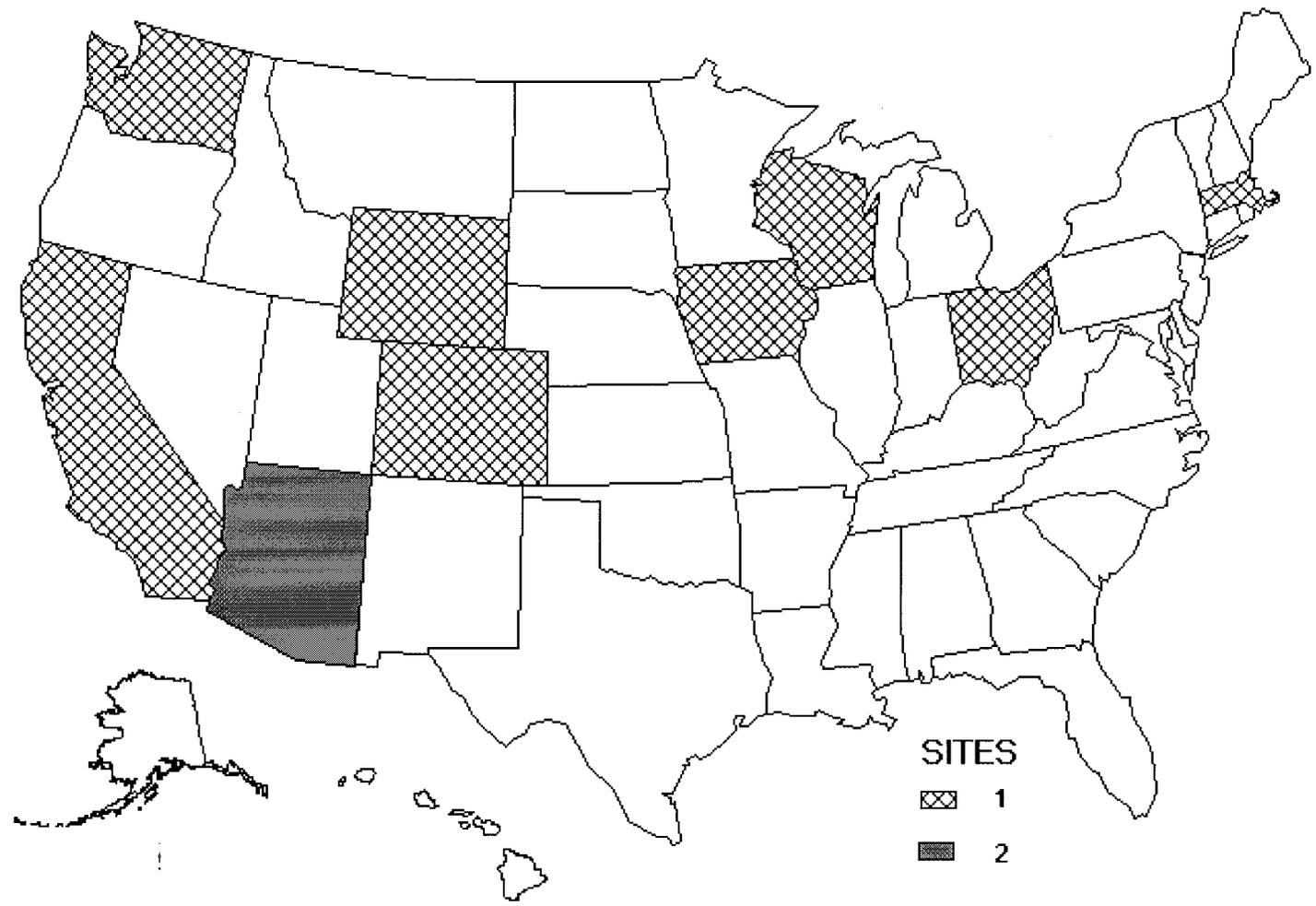
Hydraulic fluid contaminants have been identified in at least 10 of 1,428 current or former NPL Sites (HazDat 1996). All of these sites are located in the conterminous United States. The frequency of these sites can be seen in Figure 5-1. However, the number of sites evaluated for hydraulic fluids is not known.

Mineral Oil Hydraulic Fluids. Mineral oil and water-in-oil emulsion hydraulic fluids are used extensively in virtually all heavy industries as well as in construction equipment, automobiles, tractors, trucks, and material handling equipment. Potentially exposed populations include workers in heavy and allied industries and the general population due to the use of hydraulic fluids in automobiles; however, this profile does not focus on automotive fluids. The most common route of exposure is dermal contact with the neat fluid, although inhalation of oil mists and vapors may also occur. The components of mineral oil hydraulic fluids are present in many other petroleum-derived products including lubricating oils, so exposure to the major components of mineral oil hydraulic fluids is not limited to hydraulic fluid exposures.

In the past, mineral oil hydraulic fluids sometimes included additives such as polychlorinated biphenyls (PCBs) to improve the thermal resistance or other properties of the resulting fluids. These additives may present more toxicity risks than the primary ingredients of the hydraulic fluids. While such uses of PCBs have been discontinued, PCBs may be encountered as components of hydraulic fluids at NPL sites contaminated by hydraulic fluids (ATSDR 1993b).

Organophosphate Ester Hydraulic Fluids. Organophosphate ester hydraulic fluids are used in applications that require the fluid to be fire resistant, for example, in aircraft and in electrohydraulic control systems of steam turbines. It is not likely that significant concentrations in air will occur from such sources. Exposed populations include aircraft maintenance workers and mechanics, as well as other workers who maintain hydraulic control systems that use organophosphate ester hydraulic fluids. The most-common route of exposure probably is dermal contact with the neat fluid, although inhalation exposure may also occur, probably from both mists and vapors. Organophosphate esters can also enter the environment from their use as plasticizers and antiwear additives in lubricating oils. Therefore, the occurrence of organophosphate esters in the environment cannot be uniquely associated with hydraulic fluid use.

Figure 5-1. Frequency of NPL Sites with Hydraulic Fluid and Hydraulic Fluid Component Contamination



Derived from HazDat 1996

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The synthesis of organophosphate ester compounds began in the mid-1800s. From an early date, the most commercially useful compounds for lubricants, plasticizers, and hydraulic fluids were in the chemical family of the tertiary esters. Before the 1960s products were introduced based on alkyl aryl phosphates that could contain chlorinated aromatic hydrocarbons. Such products have now entirely disappeared from commercial use, and the vast majority of the industrial organophosphate esters are based on triaryl phosphates with no halogenated components (Marino 1992). However, at older waste disposal sites, hydraulic fluid site contaminants could contain chlorinated hydrocarbons. As with the PCBs formerly included as additives in other forms of hydraulic fluids, these additives may present more toxicity risks than the primary ingredients of the hydraulic fluids.

One of the main human health concerns about organophosphate esters is the potential for neurotoxicity reactions, in particular a condition known as organophosphate-induced delayed neurotoxicity (OPIDN). Tri-*ortho*-cresyl phosphate (TOCP) has been identified as one of the more potent OPIDN neurotoxins in humans, and was formerly a constituent in some organophosphate ester hydraulic fluid products (Marino 1992; Marino and Placek 1994). Production processes now routinely remove virtually all the TOCP. For instance, tricresyl phosphate (TCP) products now typically are manufactured to contain over 98% meta and para isomers and virtually no TOCP (Marino and Placek 1994). At waste disposal sites, however, site contaminants from older product formulations containing the *ortho* form may be encountered.

Polyalphaolefin Hydraulic Fluids. Polyalphaolefin hydraulic fluids are used in most applications where mineral oil fluids are used, especially those that require proper operation in cold temperatures since polyalphaolefins possess very good temperature characteristics. Exposed populations will include maintenance workers and mechanics who maintain hydraulic control systems that use polyalphaolefin hydraulic fluids. The hydrocarbon isomers of polyalphaolefin hydraulic fluids probably are also present in mineral oil, so the presence of the components of polyalphaolefins in the environment cannot be uniquely associated with polyalphaolefin hydraulic fluid usage. Nonetheless, polyalphaolefin oils have a much narrower distribution of molecular weights than mineral oils (Chrisope and Landry 1993). If, for example, there is a spill of a hydraulic fluid containing only polyalphaolefin oils, the gas chromatographic scan would be different than the scan for a similar mineral-oil-based hydraulic fluid. Polyalphaolefin oils, however, are blended with mineral oils to achieve particular properties in hydraulic fluids (Collins 1993), making it impossible to identify the presence of a polyalphaolefin oil in these cases. In addition, polyalphaolefin oils are used for applications other than hydraulic fluids, and the presence of a polyalphaolefin oil in the

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environment may result from release of a substance such as motor oil that contains polyalphaolefins, rather than hydraulic fluids.

5.2 RELEASES TO THE ENVIRONMENT

5.2.1 Air

Mineral Oil Hydraulic Fluids. The majority of the components of mineral oil and water-in-oil emulsion hydraulic fluids are not on the Toxics Release Inventory (TRI). Some water-in-oil emulsion hydraulic fluids contain ethylene glycol (Houghton 1992; Quaker 1993), which is subject to reporting under TRI. Nonetheless, since ethylene glycol is used in numerous other applications and represents $\leq 10\%$ (Houghton 1992; Quaker 1993) of the total volume of water-in-oil emulsion hydraulic fluids, it is not anticipated that TRI information concerning releases of ethylene glycol will be indicative of water-in-oil emulsion hydraulic fluid use. It may be difficult to estimate the release of mineral oil or water-in-oil emulsion hydraulic fluids to air by identifying occurrences of mineral oil (the major constituent) in air at a particular facility since mineral oils are also used in numerous other products and applications, and concentrations of the components cannot always be uniquely associated with mineral oil hydraulic fluid release.

Weschler et al. (1990) reported that the concentration of individual paraffins present in the air of a building was 0.0088-0.262 mg/m³ and was associated with operating a hydraulic elevator. Mineral oil hydraulic fluids, therefore, may be released to the air during use in hydraulic elevators (and probably other hydraulic equipment) and can come from volatilization or as mists or aerosols from fluid reservoirs and mechanisms such as actuation pistons. It is not likely that significant concentrations in air will occur from such sources.

Organophosphate Ester Hydraulic Fluids. None of the known components of organophosphate ester hydraulic fluids are on the TRI. Releases of organophosphate ester hydraulic fluids in air are probably lower than mineral oil hydraulic fluids because of their lower vapor pressures. It may be difficult to estimate the release of organophosphate ester hydraulic fluids to air by identifying occurrences of organophosphate esters (the major constituents) in air at a particular facility since organophosphate esters are also used in numerous other products and applications, and concentrations of the components cannot always be uniquely associated with organophosphate ester hydraulic fluid release.

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A component of Skydrol 500B and Skydrol LD (tributyl phosphate) was detected in the air at the CP air test facility at Vancouver International Airport at a concentration of 0.04-0.3 mg/m³ (Labour-Canada 1990), indicating that organophosphate ester hydraulic fluids may be released during aircraft maintenance operations on equipment using organophosphate ester hydraulic fluids.

Polyalphaolefin Hydraulic Fluids. None of the known components of polyalphaolefin hydraulic fluids are on the TRI. Releases of polyalphaolefin hydraulic fluids in air are probably similar to mineral oil hydraulic fluids. It may be difficult to estimate the release of polyalphaolefin hydraulic fluids to air by identifying occurrences of polyalphaolefin hydrocarbon isomers in air at a particular facility since these constituents also are present in mineral oil and concentrations of the components cannot always be uniquely associated with polyalphaolefin hydraulic fluid release. Nonetheless, the gas chromatographic profile of a polyalphaolefin will be very different than that of a mineral oil, and identification may be possible when polyalphaolefins predominate in a sample.

5.2.2 Water

Mineral Oil Hydraulic Fluids. The majority of the components of mineral oil and water-in-oil emulsion hydraulic fluids are not on the TRI. Some water-in-oil emulsion hydraulic fluids contain ethylene glycol (Houghton 1992; Quaker 1993), which is subject to reporting under the TRI. Nonetheless, since ethylene glycol is used in numerous other applications and represents $\leq 10\%$ of the total volume of water-in-oil emulsion hydraulic fluids, it is not anticipated that TRI information concerning releases of ethylene glycol will be indicative of water-in-oil emulsion hydraulic fluid use. It may be difficult to estimate the release of mineral oil or water-in-oil emulsion hydraulic fluids to water by identifying occurrences of mineral oil (the major constituent) in water at a particular facility since mineral oils also find use in numerous other products and applications, and concentrations of the components cannot always be uniquely associated with mineral oil hydraulic fluid release.

Releases of mineral oil hydraulic fluids from hydraulic systems at a steel mill were estimated to be 5,680 L/year from continuous leakage and 5,670 L/year from accidents such as line breakage (Perl et al. 1985). Spills and leakage were sent to a lagoon and then treated by a waste water treatment plant. If this amount of leakage is typical for industries using hydraulic systems, then loss of hydraulic fluids to the environment will be very large. Abdul et al. (1990) reported the spill of $\approx 208,000$ gallons of automatic

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transmission fluid (ATF) from storage tanks. The ATF migrated to groundwater. No information concerning releases from other hydraulic systems were identified in the available literature.

In the past, mineral oil hydraulic fluids sometimes included additives such as PCBs to improve the thermal resistance or other properties of the resulting fluids. While such uses of PCBs have been discontinued, PCBs may be encountered as a component of hydraulic fluids at NPL sites contaminated by hydraulic fluids (ATSDR 1993b).

Organophosphate Ester Hydraulic Fluids. None of the known components of organophosphate ester hydraulic fluids are on the TRI. Releases of organophosphate ester hydraulic fluids to water are probably similar to mineral oil hydraulic fluids. It may be difficult to estimate the release of organophosphate ester hydraulic fluids to water by identifying occurrences of organophosphate esters (the major constituents) in water at a particular facility since organophosphate esters also find use in numerous other products and applications, and concentrations of the components cannot always be uniquely associated with organophosphate ester hydraulic fluid release.

Polyalphaolefin Hydraulic Fluids. None of the known components of polyalphaolefin hydraulic fluids are on the TRI. Releases of polyalphaolefin hydraulic fluids to water are probably similar to mineral oil hydraulic fluids, only much smaller since they are not used as extensively. It should be noted that it may be difficult to estimate the release of polyalphaolefin hydraulic fluids to water by identifying occurrences of polyalphaolefin hydrocarbon isomers in water at a particular facility since these constituents also are present in mineral oil, and concentrations of the components cannot always be uniquely associated with polyalphaolefin hydraulic fluid release. Nonetheless, the gas chromatographic profile of a polyalphaolefin will be very different than that of a mineral oil, and identification may be possible when polyalphaolefins predominate in a sample.

5.2.3 Soil

Mineral Oil Hydraulic Fluids. The majority of the components of mineral oil and water-in-oil emulsion hydraulic fluids are not on the TRI. Some water-in-oil emulsion hydraulic fluids contain ethylene glycol (Houghton 1992; Quaker 1993), which is subject to reporting under TRI. Nonetheless, since ethylene glycol is used in numerous other applications and represents $\leq 10\%$ of the total volume of water-in-oil emulsion hydraulic fluids, it is not anticipated that TRI information concerning releases of ethylene glycol will be

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indicative of water-in-oil emulsion hydraulic fluid use (Houghton 1992; Quaker 1993). It may be difficult to estimate the release of mineral oil or water-in-oil emulsion hydraulic fluids to soil by identifying occurrences of mineral oil (the major constituent) in soil at a particular facility since mineral oils also find use in numerous other products and applications, and concentrations of the components cannot always be uniquely associated with mineral oil hydraulic fluid release. Abdul et al. (1990) reported that $\approx 208,000$ gallons of automatic transmission fluid (ATF) was released to soil from a leaky storage tank. Soil in the area of the spill was saturated with ATF; concentrations decreased in lower soil layers. In addition, mineral oil and water-in oil emulsion hydraulic fluids are probably released to soil from leaks and spills in a manner similar to that described by Per1 et al. (1985) for water release.

Organophosphate Ester Hydraulic Fluids. None of the known components of organophosphate ester hydraulic fluids are on the TRI. Releases of organophosphate ester hydraulic fluids to soil are probably similar to mineral oil hydraulic fluids. It may be difficult to estimate the release of organophosphate ester hydraulic fluids to soil by identifying occurrences of organophosphate esters (the major constituents) in soil at a particular facility since organophosphate esters also find use in numerous other products and applications, and concentrations of the components cannot always be uniquely associated with organophosphate ester hydraulic fluid release.

Polyalphaolefin Hydraulic Fluids. None of the known components of polyalphaolefin hydraulic fluids are on the TRI. Releases of polyalphaolefin hydraulic fluids to soil are probably similar to mineral oil hydraulic fluids. It may be difficult to estimate the release of polyalphaolefin hydraulic fluids to soil by identifying occurrences of polyalphaolefin hydrocarbon isomers in soil at a particular facility since these constituents also are present in mineral oil and concentrations of the components cannot always be uniquely associated with polyalphaolefin hydraulic fluid release. Nonetheless, the gas chromatographic profile of a polyalphaolefin will be very different than that of a mineral oil, and identification may be possible when polyalphaolefins predominate in a sample.

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5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

No information on the transport and partitioning of all the components for any of the hydraulic fluids presented in this profile was located in the available literature; thus, a full accounting of the transport and partitioning is not possible. Information is available, however, concerning the transport and partitioning of some of the major components of the hydraulic fluids, which allows an assessment of some of these components. Since hydraulic fluids are formulated to conform to performance specifications and not to specific chemical analysis, any tests performed on a specific hydraulic fluid pertain only to that particular hydraulic fluid and not necessarily to earlier or later versions of the same fluid.

Mineral Oil Hydraulic Fluids. No information identifying the major components of mineral oil or water-in-oil hydraulic fluids was located in the available literature, nor was any information located that described how the emulsifiers and other components in water-in-oil emulsion hydraulic fluids alter the environmental properties of the mineral oils contained in them. The carbon number range present in mineral oil hydraulic fluids probably is from C_{15} to C_{50} (IARC 1984; Shubkin 1993; Wills 1980). If automatic transmission fluids are typical of the mineral oil content in a hydraulic fluid, then mineral oil hydraulic fluids contain $\approx 90\%$ mineral oil (Abdul et al. 1990; Papay 1989, 1991). Therefore, the transport and partitioning of these hydrocarbons will largely account for the environmental behavior of mineral oil hydraulic fluids. Typical transport and partitioning information for hydrocarbons in this range is presented below; this information is indicative of the transport and partitioning of mineral oils present in hydraulic fluids.

The water solubility values of some C_{14-36} alkanes are presented in Table 3-7. The octanol/water partition coefficient $\log(K_{OW})$ of tetradecane (C_{14}) is 7.2 (Hutchinson et al. 1980). Water solubilities for alkanes with more than about 10-15 carbon atoms (typical of the components in gasoline) are generally considered to be low, with highest estimates at about a $\log(K_{OW})$ value of 7.4 (ATSDR 1995). Based on the available measured data, C_{15-50} alkanes as a group are expected to have low water solubilities and high K_{OW} values. In general, chemicals with low water solubilities and high K_{OW} values tend to partition to sediments when released to water and to sorb to soils (Lyman et al. 1982). Bioconcentration factors (BCFs) also tend to rise with increasing K_{OW} values, but chemicals with very high octanol/water K_{OW} values (>7) tend to have decreasing BCFs (Droy 1993). C_{15-50} hydrocarbons appear to partition to sediments and suspended particles (Bates et al. 1984; Saliot et al. 1985; Serrazanetti et al. 1991). Docosane ($C_{22}H_{46}$) has a BCF of 10,100 in

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activated sludge and 8,730 in algae (*Chlorella fusca*), but only 10 in fish (golden ide) (Freitag et al. 1985). These results for the algae and sludge may reflect a simple partitioning phenomenon more than an actual physiologically-mediated bioconcentration of the docosane. By contrast, the marine diatom *Cyclotella cryptica* has a BCF of 2 for n-C₁₆H₃₄, but the BCF dropped to 0 for C₂₈₋₃₀ hydrocarbons (Karydis 1980). In soil, C₅₋₅₀ hydrocarbons adsorbed to sludge and tended to migrate only slowly into the surrounding soil (Liu 1980). Based on the available BCF values, the hydrocarbon components of mineral oil hydraulic fluids show little tendency for bioaccumulation in animals. No studies were identified dealing with the various additives that are often associated with mineral-oil-based hydraulic fluid products.

Organophosphate Ester Hydraulic Fluids. Most of the monitoring information available for components of organophosphate ester hydraulic fluids pertains to water and sediments, with only a few reports of organophosphate esters in soils and very few reporting air or rain concentrations (see Section 5.4). There is insufficient monitoring information to demonstrate that sediments and soils are the dominant environmental sinks, as the physical/chemical properties predict.

The log K_{OW}, water solubilities, and Henry's law constants of several of the components that are present in the organophosphate ester hydraulic fluids included in this profile have been measured and are presented in Tables 3-4, 3-5, 3-8, and 3-9. In general, chemicals with low K_{OW} (log K_{OW} <1) tend to have high water solubilities, do not sorb to sediments, and do not bioconcentrate; chemicals with high K_{OW}, tend to have low water solubilities, partition to sediments and soil, and bioconcentrate in fish (Lyman et al. 1982). Most of the values presented above are for mixtures and are the average values for all of the components in the mixture.

Outdoor artificial ponds containing clay sediments (6% organic carbon, pH 6.8), fish, and chironomid larvae were treated with triphenyl phosphate, 2-ethylhexyl diphenyl phosphate, t-butylphenyl diphenyl phosphate, and tri(*m*-cresyl) phosphate and their concentration and partitioning monitored over time (Muir et al. 1985). After 18 hours, 62.3%, 61.5%, and 77.7% of the applied radioactivity was present in the sediment for 2-ethylhexyl diphenyl phosphate (labeled at C₁), t-butylphenyl diphenyl phosphate (ring labeled), and tri(*m*-cresyl) phosphate (ring-labeled), respectively. After 18 hours, ≈ 24% of the applied radioactivity was present in the water for all esters, and 1.3-1.8% of the applied radioactivity was present in the biota. After 7 days, concentrations in the biota were ≤0.5%; and after 21 days, concentrations in the biota were below the detection limit (≤0.1 % or 0.2 mg). Sediment concentrations also dropped over time, although much more slowly. After 360 days, 23.6-30.5% of the applied radioactivity was still present in the sediments and was present at least to some extent as untransformed ester, as determined by gas chromatographic analyses. Air

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concentrations measured at 5 cm above the ponds decreased from maximum concentrations of 1.97×10^{-4} and 3.2×10^{-5} mg/m³ measured in the first 18 hours for t-butylphenyl diphenyl phosphate and 2-ethylhexyl diphenyl phosphate, respectively, to below 2×10^{-6} mg/m³ after 3 days. By contrast, in a more complex artificial pond containing clay sediments (6% organic matter, pH 6.8), fish (rainbow trout), duckweed, and cattails, 32% and 34% of the applied radioactivity of 2-ethylhexyl diphenyl phosphate and triphenyl phosphate, respectively, was present in the sediments after 24 hours, while 36% and 52%, respectively, was in the water (Muir et al. 1982). Over the course of the experiment (240 hours), the cattails never absorbed a measurable amount of radioactivity (0.2%), while the duckweed and fish absorbed 1.4-1.7% and 2.0-3.4%, respectively, of the applied radioactivity in 24 hours. After 240 hours, the duckweed and fish contained 0.2-0.5% and 3.0-0.5%, respectively, of the applied radioactivity (the amount of radioactivity in the fish appeared to be decreasing during the experiment, but increased from 0.2% to 3.0% between 180 and 240 hours for 2-ethylhexyl diphenyl phosphate). A study was conducted by Mayer et al. (1981) on the transport and partitioning of Pydraul50E in a lake microcosm containing 8 L of sediment and 20 L of water. At the end of the 28-day test, 38-47% of the originally applied Pydraul 50E remained in the sediment. In the materials that remained in the sediment, about 10% was triphenyl phosphate, and approximately 90% was nonylphenyl diphenyl phosphate and cumylphenyl diphenyl phosphate. Significant degradation occurred in this system after 28 days. These results show that, in general, the higher molecular weight fractions of the organophosphate ester hydraulic fluids partition to the sediments, while lower molecular weight fractions tend to remain in the water column or degrade.

The BCFs of some of the components of organophosphate ester hydraulic fluids are presented in Table 5-1. In general, the larger organophosphate esters, such as cumylphenyl diphenyl phosphate, concentrate more in fish because they have higher K_{OW} values and hence, tend to partition to fat, while smaller ones, such as triphenyl phosphate, concentrate less because they have lower K_{OW} values and do not partition. In fish, organophosphate esters appear to be more bioavailable when sediments are not present (Huckins et al. 1991), but chironomids appear to be able to bioaccumulate organophosphate esters from the sediments (Muir et al. 1983b, 1985).

Polyalphaolefin Hydraulic Fluids. The transport and partitioning properties of the polyalphaolefin hydraulic fluids will be similar to the mineral oil fluids since they contain similar aliphatic hydrocarbon isomers.

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Table 5-1. Bioconcentration Factors for Components of Organophosphate Ester Hydraulic Fluids

Organophosphate ester	Rainbow fathead trout	Minnows	Reference
<i>t</i> -Butylphenyl diphenyl phosphate	1,096	785	Muir et al. 1983 ^a
Cumylphenyl diphenyl phosphate	2,807		Mayer et al. 1981 ^a
Cumylphenyl diphenyl phosphate	1,156		Lombardo and Egry 1979 ^b
Nonylphenyl diphenyl phosphate	133		Lombardo and Egry 1979 ^b
Nonylphenyl diphenyl phosphate	691		Mayer et al. 1981 ^a
Tricresyl phosphate (mixture)	165		Veith et al. 1979 ^b
<i>m</i> -Tricresyl phosphate	784	596	Muir et al. 1983 ^a
<i>p</i> -Tricresyl phosphate	1,420	928	Muir et al. 1983 ^a
Triphenyl phosphate	216		Lombardo and Egry 1979 ^b
Triphenyl phosphate	271		Mayer et al. 1981 ^a
Triphenyl phosphate	573	561	Muir et al. 1983 ^a

^aStatic test method^bFlow-through test method

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5.3.2 Transformation and Degradation

5.3.2.1 Air

Mineral Oil Hydraulic Fluids. No information concerning the atmospheric transformation and degradation of C₁₇₋₅₀ hydrocarbons was found in the available literature. Alkanes degrade in the atmosphere by reacting with hydroxyl radicals via hydrogen abstraction; reaction rates for *n*-alkanes increase with increasing chain length because more hydrogen ions are available for removal. Reaction rates for C₁₀₋₁₆ hydrocarbons are (11.7-25.0) × 10⁻¹² cm³ s⁻¹ (at 300 K) (Nolting et al. 1988), corresponding to gas phase half-lives of 0.6-1.4 days for average hydroxyl radical concentrations of 0.5 × 10⁻⁶ molecules cm⁻³. A study conducted by Cautreels and Van Cauwenberghe (1978) reported that C₂₅₋₃₁ hydrocarbons were 1-3 times more likely to be associated with particulates than with the gas phase, so the actual atmospheric half-life of these hydrocarbons may be longer.

Organophosphate Ester Hydraulic Fluids. No information concerning the atmospheric transformation and degradation of organophosphate ester hydraulic fluids was found in the available literature.

Polyalphaolefin Hydraulic Fluids. The transformation and degradation properties of the polyalphaolefin hydraulic fluids in air will be similar to the mineral oil fluids since they contain similar hydrogen isomers.

5.3.2.2 Water

Mineral Oil Hydraulic Fluids. In water, low concentrations of C₁₅₋₅₀ hydrocarbons will biodegrade. Haines and Alexander (1974) reported that C₁₆₋₄₄ hydrocarbons degraded in a soil-water suspension (64-71% degradation in 20 days), while Matsumoto (1983) reported that river water highly polluted with sewage degraded *n*-alkanes (>90% in 29 days) faster than branched alkanes. While these data indicate that C₁₅₋₃₀ hydrocarbons will biodegrade, no information is available that will allow an estimation of the rates of degradation in the environment or an estimation of any attenuating or accelerating effects other mineral oil hydraulic fluid components may have on degradation.

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Organophosphate Ester Hydraulic Fluids. Numerous reports are available detailing the aerobic biodegradation of organophosphate esters. These reports indicate that organophosphate esters will degrade with half-lives of a few days to several months under aerobic conditions, using a river die-away test. (A river die-away test is a very common biodegradation test in which river or lake water is spiked with a chemical of interest, and the concentration of the chemical is monitored with time. This type of test is more indicative of degradation in natural systems than tests using, for example, pure cultures or sludge inocula.) Results vary depending on the organophosphate used and the exact conditions of the test; triphenyl phosphate appears to degrade rapidly while more complex organophosphate esters degrade slowly (FMC 1978b; Heitkamp et al. 1986; Howard and Deo 1979; Mayer et al. 1981; Monsanto 1978, 1983a, 1983b, 1983c; Saeger et al. 1979). Specific complex esters for which river die-away test information is available include butyl diphenyl phosphate, *tert*-butylphenyl diphenyl phosphate, dibutyl phenyl phosphate, nonylphenyl diphenyl phosphate, and cumylphenyl phosphate. Similar half-lives are expected in the environment.

Under sewage treatment plant conditions, organophosphate ester components of hydraulic fluids may not completely degrade, depending on the influent concentration. Some organophosphate esters were toxic to sludge microorganisms especially at feed rates of 13 mg/L, while lower feed rates were degraded 74-99% in 24 hours (Saeger et al. 1979).

Hydrolysis appears to be the most important abiotic degradative mechanism for organophosphate esters under basic pH conditions. Under neutral and acidic conditions, the reaction slows considerably and could become an insignificant removal mechanism. The hydrolysis proceeds by a stepwise mechanism in which one alcohol group is removed at a time. The first step is cleavage of a P-OR bond (where "R" is an aryl or alkyl group) to produce a diester of phosphoric acid, which, under basic conditions, becomes an anion. This anion is much more resistant to further hydrolytic cleavage than the triester (Barnard et al. 1961). This property of organophosphate esters may be of environmental importance since phosphoric acid diesters are much more soluble and very little is known concerning the environmental toxicity of these compounds. The available data do not provide sufficient descriptions of the experimental methods to determine if the rates are reliable (Barnard et al. 1961; Ciba-Geigy 1984e, 1986; Howard and Deo 1979; Mayer et al. 1981; Wolfe 1980). The majority of reports provide only a minimum of information and exclude important facts such as the duration of the experiments and the concentration of buffers. Despite the lack of experimental detail, published rate constants for base-catalyzed hydrolysis appear to be reasonably consistent and suggest that the hydrolytic half-life of triphenyl phosphate will vary from 350 days at pH 6.0 to 9.3 days at pH 8.5. Rates for tricresyl

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phosphate appear to be on the same order as for triphenyl phosphate. Other alkylphenyl diphenyl phosphates appear to have rates about an order of magnitude smaller than triphenyl phosphate and tricresyl phosphate.

Polyalphaolefin Hydraulic Fluids. The transformation and degradation properties of the polyalphaolefin hydraulic fluids in water will be similar to the mineral oil fluids since they contain similar aliphatic hydrocarbon isomers.

5.3.2.3 Sediment and Soil

Mineral Oil Hydraulic Fluids. No information concerning the transformation and degradation of mineral oil hydraulic fluids in sediments and soils was found in the available literature.

Organophosphate Ester Hydraulic Fluids. Sediment degradation of organophosphate ester hydraulic fluid components was studied by Mayer et al. (1981) and Muir et al. (1982, 1985) in microcosms as described in Section 5.3.1. In general, these authors found that organophosphate esters partitioned to the sediments where degradation (presumably biodegradation) occurred slowly. Larger organophosphate esters degraded more slowly. The pseudo-first-order half-lives for t-butylphenyl diphenyl phosphate, cumylphenyl diphenyl phosphate, and tricresyl phosphate in sediment were 39, 79, and 39 days, respectively (Muir et al. 1985). Rates are expected to be dependent on environmental conditions such as temperature, contaminants, nutrients, and pre-exposure of the system to organophosphorus esters.

While there is little information identified in the literature on empirical laboratory studies documenting disappearance rates in microcosms for organophosphate esters, one study (Heltkamp et al. 1984) provides results on degradation of the triaryl organophosphate known as isopropylphenyl diphenyl phosphate (IPDP). Results for both aerobic and anaerobic sediment microcosms showed a disappearance of less than 8% from the initial IPDP concentration levels after 4 weeks due to a combination of physical and biochemical degradation. IPDP is a common type of organophosphate ester, whose production has increased because of concerns over possible toxic impacts from tricresyl organophosphates and cresyl diphenyl organophosphates (Heltkamp et al. 1984).

Studies conducted by Pickard et al. (1975) documented that bacteria can use triaryl phosphate-containing hydraulic or lubricating fluids as a carbon source. An inoculum of a mixed bacterial population was obtained from lake sediments that had a history of spills from aviation fuels and other petrochemical oils.

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Tests showed cell growth on a commercial triaryl phosphate lubricating oil (Fyrquel 220) (0.5% TOCP by weight) and on its individual components, triphenyl phosphate, tri-*ortho*-cresyl phosphate and trixylenyl phosphate. The bacteria were able to emulsify the substrate, which increased the surface area and otherwise enhanced the conditions needed for actual biodegradation of the triaryl phosphates. Actual biodegradation, as reflected in cell growth, was still considered very low. The ability of the bacteria to emulsify the substrate, however, could accentuate chemical degradation processes such as hydrolysis (see Section 5.3.2.2 above).

Polyalphaolefin Hydraulic Fluids. No information concerning the transformation and degradation of polyalphaolefin hydraulic fluids in sediments and soils was found in the available literature.

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

5.4.1 Air

Mineral Oil Hydraulic Fluids. It is difficult to assess the presence of mineral oil or water-in-oil emulsion hydraulic fluids in air by identifying occurrences of mineral oil (the major constituent) in air since mineral oils are also used in numerous other products and applications and these other applications account for a much greater volume than hydraulic fluid applications. For example, the National Petroleum Refiners Association (NPRA) reported that over 1 billion gallons of mineral-oil-based engine oils were sold in the United States every year from 1984 to 1991; this volume does not account for other mineral-oil-based products such as gear oils or other consumer, industrial, or commercial oil products (NPRA 1992). By contrast, only \approx 200 million gallons of mineral oil and water-in-oil emulsion hydraulic fluids were sold each year between 1984 and 1991 (NPRA 1992). Thus, even if mineral oil or water-in-oil emulsion losses from hydraulic fluid were much greater on a percentage basis than losses from engine oils, because of the very large differences in use volumes, it would still be difficult to associate the occurrence of mineral oil in air with hydraulic fluid usage.

Organophosphate Ester Hydraulic Fluids. Organophosphate esters are used in numerous applications other than hydraulic fluids including use as flame retardant plasticizers and antiwear additives to lube oils (FMC 1991c, 1991d, 1992c, 1992d; Weil 1980); no current estimates are available concerning the amounts of organophosphate esters used for these applications. Plasticizer applications include electrical insulation, automotive interiors, furniture upholstery, conveyor belts, and vinyl foams (Weil 1980), and some emissions to the air are expected from these uses. Therefore, organophosphate ester occurrence in air will be

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associated with hydraulic fluid, engine oil, plasticizer, and other uses. No reports of organophosphate ester occurrence in air were located in the available literature and only one report was found for occurrence in rainwater. Kawamura and Kaplan (1983) reported that unspecified concentrations of triphenyl phosphate and tributyl phosphate were detected in rainwater in Los Angeles.

Polyalphaolefin Hydraulic Fluids. As is the case with mineral oil hydraulic fluids, assessing the presence of polyalphaolefin hydraulic fluids in air by identifying occurrences of the components of these hydraulic fluids may be difficult because the hydrocarbon isomers in polyalphaolefin hydraulic fluids also are present in mineral oils. Thus, the occurrence of polyalphaolefins in air cannot always be uniquely associated with hydraulic fluid usage.

5.4.2 Water

Mineral Oil Hydraulic Fluids. It is difficult to assess the presence of mineral oil or water-in-oil emulsion hydraulic fluids in water by identifying occurrences of mineral oil in water since mineral oils also find use in numerous other products and applications, which account for a much greater volume than hydraulic fluid applications. For example, NPRA (1992) reported that over 1 billion gallons of mineral-oil-based engine oils were sold in the United States every year from 1984 to 1991 and this volume does not account for other mineral-oil-based products such as gear oils or other consumer, industrial, or commercial oil products. By contrast, only \approx 200 million gallons of mineral oil and water-in-oil emulsion hydraulic fluids were sold each year between 1984 and 1991 (NPRA 1992). Thus, even if mineral oil or water-in-oil emulsion losses from hydraulic fluid were much greater on a percentage basis than losses from engine oils, because of the very large differences in use volumes, it would still be difficult to associate the occurrence of mineral oil in the environment with hydraulic fluid usage. In addition, \approx 193 million gallons of do-it-yourself-generated used oils are disposed of annually (EPA 1992a), which is approximately equal to the entire sales volume of mineral oil and water-in-oil emulsion hydraulic fluids. Since do-it-yourself-generated used oils are not widely recycled, but disposed of in other ways (EPA 1992a), it is more likely that occurrences of mineral oil in water will be associated with engine oils than with hydraulic fluids. -.

Abdul et al. (1990) reported that groundwater was contaminated with automatic transmission fluid (ATF) after a storage tank leaked \approx 208,000 gallons onto the surrounding soil. Pure ATF penetrated the saturated zone and migrated with groundwater flow from there, saturating surrounding groundwater.

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Organophosphate Ester Hydraulic Fluids. Organophosphate esters are used in numerous applications other than hydraulic fluids including use as flame retardant plasticizers and antiwear additives to lube oils (FMC 1991 c, 1991 d, 1992c, 1992d; Weil 1980); no current estimates are available concerning the amounts of organophosphate esters used for these applications. Plasticizer applications include electrical insulation, automotive interiors, furniture upholstery, conveyor belts, and vinyl foams (Weil 1980), and some emissions to the water are expected from these uses. Therefore, organophosphate ester occurrence in water will be associated with hydraulic fluid, engine oil, and plasticizer use.

Data show that organophosphate esters, while not ubiquitous in surface waters, are geographically widespread contaminants and appear to be present principally in industrialized locations, especially where organophosphate esters are manufactured. In nonpolluted areas, concentrations typically are $<1 \mu\text{g/L}$, but in polluted areas, concentrations appear to be in the range of $\approx 1\text{-}10 \mu\text{g/L}$ (Deleon et al. 1986; EPA 1978, 1979a; FMC 1977c, 1979, 1980; Konasewich et al. 1978; Mayer et al. 1981; Monsanto 1981; Sheldon and Hites 1978, 1979; Strachan 1974; Weber and Ernst 1983); however, concentrations $\leq 29.5 \mu\text{g/L}$ have been reported (Keith et al. 1976; LeBel et al. 1981; Mayer et al. 1981; Suffet et al. 1980; Williams et al. 1982). For example, FMC (1979, 1980) reported that surface water concentrations of organophosphate esters were generally below the detection limit upstream of their Nitro, West Virginia, plant near the Kanawha River (where organophosphate esters are produced), while concentrations of $0.1\text{-}4.2 \mu\text{g/L}$ were detected downstream of the plant. Similarly, Mayer et al. (1981) found $<0.1 \mu\text{g/L}$ of nonylphenyl diphenyl phosphate and cumylphenyl diphenyl phosphate at 9 of 10 locations throughout the midwest and San Francisco, but found $2\text{-}20 \mu\text{g/L}$ in 3 of 15 samples taken near Monsanto's St. Louis organophosphate ester manufacturing facility. Thus, organophosphate esters are present in surface waters, particularly near manufacturing and use facilities, but the data suggest that they disappear rapidly from the water column by degradation or by partitioning to sediments, as indicated from the data presented in Sections 5.3.1 and 5.3.2.

Organophosphate ester hydraulic fluid components have also been detected in groundwater near a hazardous waste site ($1.7 \mu\text{g/L}$ tributyl phosphate) (Sawhney 1989) and in surface water from a radioactive waste disposal site (triphenyl phosphate and tributyl phosphate) (Francis et al. 1980). Organophosphate ester components of hydraulic fluids also have been detected in drinking water from New Orleans, the Great Lakes, and Philadelphia (Keith et al. 1976; LeBel et al. 1981; Suffet et al. 1980; Williams et al. 1982).

Concentrations of $0.03\text{-}1.31 \mu\text{g/L}$ in finished water from New Orleans have been reported, and concentrations $\leq 29.5 \mu\text{g/L}$ in raw water taken from the Great Lakes have been reported. All finished water from six Ontario drinking water plants drawing their water from the Great Lakes contained tributyl and

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triphenyl phosphates (0.2-11.8 ng/L) while tricresyl phosphate was detected in water from one plant (LeBel et al. 1981).

Polyalphaolefin Hydraulic Fluids. As is the case with mineral oil hydraulic fluids, assessing the presence of polyalphaolefin hydraulic fluids in water by identifying occurrences of the components of these hydraulic fluids is difficult because the aliphatic hydrocarbon isomers in polyalphaolefin hydraulic fluids also are present in mineral oils. Thus, the occurrence of polyalphaolefins in water cannot always be uniquely associated with hydraulic fluid usage.

5.4.3 Sediment and Soil

Mineral Oil Hydraulic Fluids. It is difficult to assess the presence of mineral oil or water-in-oil emulsion hydraulic fluids in sediments and soil by identifying occurrences of mineral oil in sediments and soil since mineral oils also find use in numerous other products and applications and these other applications account for a much greater volume than hydraulic fluid applications. For example, NPRA (1992) reported that over 1 billion gallons of mineral-oil-based engine oils were sold in the United States every year from 1984 to 1991, and this volume does not account for other mineral-oil-based products such as gear oils or other consumer, industrial, or commercial oil products. By contrast, only ≈ 200 million gallons of mineral oil and water-in-oil emulsion hydraulic fluids were sold each year between 1984 and 1991 (NPRA 1992). Thus, even if mineral oil or water-in-oil emulsion losses from hydraulic fluid were much greater on a percentage basis than losses from engine oils, because of the very large differences in use volumes, it would still be difficult to associate the occurrence of mineral oil in the environment with hydraulic fluid usage. In addition, ≈ 193 million gallons of do-it-yourself-generated used oils are disposed of annually (EPA 1992a), which is approximately equal to the entire sales volume of mineral oil and water-in-oil emulsion hydraulic fluids. Since do-it-yourself-generated used oils are not widely recycled, but disposed of in other ways (EPA 1992a), it is more likely that occurrences of mineral oil in sediments and soil will be associated with engine oils than with hydraulic fluids.

Abdul et al. (1990) reported that upper layers of soil were saturated with automatic transmission fluid (ATF) after a storage tank leaked $\approx 208,000$ gallons onto the surrounding soil. Lower soil layers contained less ATF; volumetric ATF concentrations ranged from $<10\%$ to 40% at 80-0 cm above the ATF table.

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Organophosphate Ester Hydraulic Fluids. Organophosphate esters are used in numerous applications other than hydraulic fluids including use as flame retardant plasticizers and antiwear additives to lube oils (FMC 1991c, 1991 d, 1992c, 1992d; Weil 1980); no current estimates are available concerning the amounts of organophosphate esters used for these applications. Plasticizer applications include electrical insulation, automotive interiors, furniture upholstery, conveyor belts, and vinyl foams (Weil 1980), and some emissions to the soil and sediment are expected from these uses. Therefore, organophosphate ester occurrence in soils and sediment will be associated with hydraulic fluid, engine oil, and plasticizer use.

Sediment monitoring data present a different picture than the water monitoring data discussed above. For most cases in which organophosphate esters were detected in water, concentrations many times higher were found in the sediment (Adams et al. 1986; EPA 1978, 1979a; FMC 1977c; Konasewich et al. 1978; Mayer et al. 1981). The concentration factors ranged from around 100 to $>10^8$. This is expected, based on the $10g K_{OW}$ for these chemicals. When detected, sediment concentrations were in the range of <100 to $>6,300,000 \mu\text{g/L}$. While not ubiquitous, detectable concentrations in the sediment were found in more locations than concentrations in water, indicating a more widespread release than would be expected from the water monitoring data alone. These data also support the indication of microcosm studies (see Sections 5.3.1 and 5.3.2) that the water column rapidly loses detectable concentrations of organophosphate esters to the sediments, which accumulate the esters. The data further show that concentrations of triphenyl phosphate in the environment are lower than concentrations of other organophosphate esters. This agrees with the data presented above, which indicate that triphenyl phosphate degrades more rapidly than the other organophosphate esters.

Typical concentrations are more difficult to determine for sediments than for water since the range of reported values is very large, and most of the monitoring is not random but centered around manufacturing facilities (sediment concentrations are not limited by the solubility of the organophosphate esters as are water concentrations). In the sediment, concentrations appear to drop off rapidly with distance from the source (FMC 1979, 1980). This further indicates that sorption to sediments is rapid as well as thermodynamically favored. Monitoring studies of the Kanawha River in Nitro, West Virginia, by FMC (1980) revealed unspecified aryl phosphates at 7,200-6,320,000 $\mu\text{g/kg}$ within 800 yards of the plant outfall. Mayer et al. (1981) reported sediment concentrations in the range of 10-20,000 pg/kg in a variety of locations. Higher sediment concentrations are also commonly reported. Both tricresyl phosphate and isopropylphenyl diphenyl phosphate were detected at 5,000 $\mu\text{g/kg}$ in sediment from Bethlehem, Pennsylvania, where fire resistant

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hydraulic fluids are used in steel mills (EPA 1979a). Organophosphate esters were detected at 1,580,000 ug/kg in sediment samples from Kishacoquillas Creek, Pennsylvania (Sheaffer 1977).

Polyalphaolefin Hydraulic Fluids. As is the case with mineral oil hydraulic fluids, it may be difficult to assess the presence of polyalphaolefin hydraulic fluids in sediments and soil by identifying occurrences of the components of these hydraulic fluids, because the aliphatic hydrocarbon isomers in polyalphaolefin hydraulic fluids also are present in mineral oils. Thus, the occurrence of polyalphaolefins in sediments and soil cannot always be uniquely associated with hydraulic fluid usage.

5.4.4 Other Environmental Media

Mineral Oil Hydraulic Fluids. It is difficult to assess the presence of mineral oil or water-in-oil emulsion hydraulic fluids in other environmental media by identifying occurrences of mineral oil (the major constituent) in other environmental media since mineral oils also find use in numerous other products and applications and these other applications account for a much greater volume than hydraulic fluid applications. For example, NPRA (1992) reported that over 1 billion gallons of mineral-oil-based engine oils were sold in the United States every year from 1984 to 1991, and this volume does not account for other mineral-oil-based products such as gear oils or other consumer, industrial, or commercial oil products. By contrast, only \approx 200 million gallons of mineral oil and water-in-oil emulsion hydraulic fluids were sold each year between 1984 and 1991 (NPRA 1992). Thus, even if mineral oil or water-in-oil emulsion losses from hydraulic fluid were much greater on a percentage basis than losses from engine oils, because of the very large differences in use volumes, it would still be difficult to associate the occurrence of mineral oil in the environment with hydraulic fluid usage. In addition, \approx 193 million gallons of do-it-yourself-generated used oils are disposed of annually (EPA 1992a), which is approximately equal to the entire sales volume of mineral oil and water-in-oil emulsion hydraulic fluids. Since do-it-yourself-generated used oils are not widely recycled, but disposed of in other ways (EPA 1992a), it is more likely that occurrences of mineral oil in other environmental media will be associated with engine oils than with hydraulic fluids. No literature was identified dealing explicitly with the bioavailability of mineral-oil-based hydraulic fluids.

Organophosphate Ester Hydraulic Fluids. Organophosphate esters are used in numerous applications other than hydraulic fluids including use as flame retardant plasticizers and antiwear additives to lube oils (FMC 1991c, 1991d, 1992c, 1992d; Weil 1980); no current estimates of the amounts of organophosphate esters used for these applications are available. Plasticizer applications include electrical

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insulation, automotive interiors, furniture upholstery, conveyor belts, and vinyl foams (Weil 1980), and some uptake by other environmental media are expected from these uses. Therefore, organophosphate ester occurrence in other environmental media will be associated with hydraulic fluid, engine oil, and plasticizer use.

Organophosphate esters have also been detected in vegetation around manufacturing and use facilities and in sewage sludge. The detection of organophosphate esters on vegetation suggests that when emitted, organophosphate esters are present as aerosols that deposit in detectable concentrations near the site of origin (EPA 1978, 1979a). Positive detections on vegetation ranged from 1,000 to 20,000 ppb, while soil concentrations ranged from 100 to 400,000 ppb (EPA 1978, 1979a). The presence of organophosphate esters in sewage sludge (Konasewich et al. 1978) indicates that these compounds are not always degraded in sewage treatment plants, but removal from the influent water may be accomplished by a combination of sorption and degradation. Landfilling of the sludge may result in a more widespread distribution of these compounds in the environment since municipal waste landfills are sometimes used to dispose of sewage sludge and these landfills are not always lined with materials that prevent leaching and/or runoff.

Nonetheless, many organophosphate esters are strongly sorbed to sludge and will not be subject to leaching or run off.

Organophosphate ester components of hydraulic fluids such as triphenyl phosphate, nonylphenyl diphenyl phosphate, and cumylphenyl phosphate also have been detected in fish; concentrations of 0.1-0.9 $\mu\text{g/g}$ of fish tissue were detected principally near manufacturing facilities, while fish caught in other areas generally had concentrations below the detection limit (0.1 $\mu\text{g/g}$) (Mayer et al. 1981). In a market basket survey, tributyl phosphate was found to be present in 2% of the foods analyzed between April 1982 and April 1984 (Gunderson 1988). Intakes of tributylphosphate were estimated to be a maximum of 38.9 ng/kg body weight/day for 6- to 11 -month-old children.

Polyalphaolefin Hydraulic Fluids. As is the case with mineral oil hydraulic fluids, assessing the presence of polyalphaolefin hydraulic fluids in other environmental media by identifying occurrences of the components of these hydraulic fluids may be difficult because the aliphatic hydrocarbon isomers in polyalphaolefin hydraulic fluids also are present naturally in mineral oils. Thus, the occurrence of polyalphaolefins in other environmental media cannot always be uniquely associated with hydraulic fluid usage.

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5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Mineral Oil Hydraulic Fluids. Mineral oil and water-in-oil hydraulic fluids comprise the largest category of hydraulic fluids under consideration. These fluids include automobile automatic transmission fluids and power steering fluids as well as fluids used in many industrial and commercial applications. Because of this, extremely widespread general population, occupational, and military exposure to these fluids is expected, including exposures of automobile, truck, and tractor mechanics and workers in any heavy or light industry that makes use of hydraulic equipment (including forklift trucks, construction equipment, and farm equipment). While estimates of the numbers of persons occupationally exposed were not located in the available literature, the number of workers exposed will be extremely high, since mineral oil hydraulic fluids are used in virtually all heavy industry. No recent estimates were found that quantified the general population exposure to mineral oil hydraulic fluids from do-it-yourself operations; however, the numbers may be very large. Exposure will probably occur by both dermal contact and inhalation.

Weschler et al. (1990) reported that the concentration of individual paraffins present in the air of a building was 0.0088-0.262 mg/m³ and was associated with operating a hydraulic elevator.

Organophosphate Ester Hydraulic Fluids. Organophosphate ester hydraulic fluids are used in applications that require a degree of fire resistance such as in aircraft. EPA (1992b) has noted that aircraft mechanics may have dermal exposures of 1,300-3,900 mg/day and that 2,200 aircraft workers are routinely exposed to tributyl phosphate, while another 43,000 mechanics may be exposed at various times. Estimates of worker exposure in other industries were not found in the available literature. General population and military personnel exposure to organophosphate ester hydraulic fluids is likely to be much lower than exposure to mineral oil hydraulic fluids because these fluids have more specialized uses.

A component of Skydrol 500B and Skydrol LD (tributyl phosphate) was detected in the air at the CP air test facility at Vancouver International Airport at a concentration of 0.04-0.3 mg/m³ (Labour Canada 1990), indicating that organophosphate ester hydraulic fluids may be released during aircraft maintenance operations on equipment using organophosphate ester hydraulic fluids.

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Polyalphaolefin Hydraulic Fluids. Polyalphaolefin hydraulic fluids find significant use in a number of applications including situations where cold temperature operation is important. Applications include construction equipment and other machinery that is designed to operate in cold conditions. No estimates of either occupational or general population exposure to these hydraulic fluids were found in the available literature.

5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Mineral Oil Hydraulic Fluids. Populations with potentially high exposures to mineral oil hydraulic fluids include all occupations that maintain hydraulic equipment including automobile, truck, and tractor mechanics, mechanics employed by heavy industry and mining operations to repair and maintain hydraulic equipment, and other maintenance workers involved with the repair and maintenance of hydraulic systems. The number of workers with potentially high exposures to mineral oil hydraulic fluids is expected to be very large.

Organophosphate Ester Hydraulic Fluids. Populations with potentially high exposures to organophosphate ester hydraulic fluids include aircraft mechanics and other mechanics repairing and maintaining hydraulic equipment designed to operate near combustion sources that require fire resistant hydraulic fluids.

Polyalphaolefin Hydraulic Fluids. Populations with potentially high exposures to polyalphaolefin hydraulic fluids include mechanics repairing and maintaining hydraulic equipment containing polyalphaolefin hydraulic fluids, including military personnel using or repairing equipment having these fluids.

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 hydraulic fluids is available. Where adequate information is not available, ATSDR, in conjunction with the 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 hydraulic fluids.

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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 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 will be proposed.

57.1 Identification of Data Needs

Most hydraulic fluid preparations start as chemical mixtures. For instance, there is a considerable area of overlap in the specific petroleum hydrocarbon chemicals contained in the mineral oil and polyalphaolefin hydraulic fluids. For all classes of hydraulic fluids, there may be similarities with other original products intended for use as lubricants. The complications involved in documenting the environmental fate of mixtures increase under conditions encountered at many NPL sites, where it may be hard to determine the precise original product associated with chemicals identified at an area in need of remediation. In most instances, available peer-reviewed literature, supplemented with data obtained from manufacturers of particular formulations and information in trade magazines, can supply information about the original hydraulic fluid preparations. At NPL sites, site-specific evaluations of specific chemicals may be the only feasible way to address concerns over environmental fate and potential exposure risks.

In the sections that follow, the data needs issues for the mineral oil and polyalphaolefin hydraulic fluids will be discussed first. This will be followed in each section by a discussion of issues regarding organophosphate ester-based products.

Physical and Chemical Properties.

Mineral Oil Hydraulic Fluids and Polyalphaolefin Hydraulic Fluids. Limited information about environmentally important physical and chemical properties is available for the mineral oil and water-in-oil emulsion hydraulic fluid products and components is presented in Tables 3-4, 3-5, and 3-7. Much of the available trade literature emphasizes properties desirable for the commercial end uses of the products as hydraulic fluids rather than the physical constants most useful in fate and transport analysis. Since the products are typically mixtures, the chief value of the trade literature is to identify specific chemical components, generally various petroleum hydrocarbons. Additional information on the properties of the various mineral oil formulations would make it easier to distinguish the toxicity and environmental effects

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and to trace the site contaminant's fate based on levels of distinguishing components. Improved information is especially needed on additives, some of which may be of more environmental and public health concern than the hydrocarbons that comprise the bulk of the mineral oil hydraulic fluids by weight. For the polyalphaolefin hydraulic fluids, basic physical and chemical properties related to assessing environmental fate and exposure risks are essentially unknown. Additional information for these types of hydraulic fluids is clearly needed.

Organophosphate Ester Hydraulic Fluids. The physical and chemical property information available for the organophosphate ester hydraulic fluid products and components is presented in Tables 3-4, 3-5, 3-8, and 3-9. Much of this information was abstracted from trade literature or data taken from material safety data sheets. While there is information on many of the major component chemicals in the hydraulic fluid products, there can still be major data uncertainties for products that involve mixtures of different components. While current manufacturing practices aim to minimize or eliminate the presence of such worrisome components as tri-*ortho*-cresyl phosphate, there remain major uncertainties about the composition and properties of older products, which would be more commonly encountered as site contaminants at NPL sites. Additional information on physical and chemical properties for organophosphate ester hydraulic fluid products is, therefore, an important data need.

Production, Import/Export, Use, Release, and Disposal. According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit chemical release and off-site transfer information to the EPA. The Toxics Release Inventory (TRI), which contains this information for 1993, became available in May of 1995. This database will be updated yearly and should provide a list of industrial production facilities and emissions. However, most of the components contained in hydraulic fluids are not on the Toxics Release Inventory (TRI) (EPA 1995).

Mineral Oil Hydraulic Fluids and Polyalphaolefin Hydraulic Fluids. Very little public information is collected on the production volume and methods, import/export, applications, and disposal practices for the different types of mineral oil and polyalphaolefin hydraulic fluids. This is largely because public data series will generally not distinguish between hydraulic fluids and lubricants. Because of the extremely large number of workers and people in the general population exposed to these hydraulic fluids, development of more carefully defined data would allow a more accurate estimate of the numbers of people exposed and would allow development of likely routes of exposure and environmental loss.

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Organophosphate Ester Hydraulic Fluids. Very little is known about the production volume, import/export, and disposal practices for the different types of organophosphate ester hydraulic fluids. Because of the large number of workers exposed to these hydraulic fluids, development of these data would allow a much more accurate estimate of the numbers of people exposed, and would allow development of likely routes of exposure and environmental loss.

Environmental Fate.

Mineral Oil Hydraulic Fluids and Polyalphaolefin Hydraulic Fluids. Very little direct information is available concerning the environmental fate of these categories of hydraulic fluids. Especially at NPL sites, the identity of the original products may be uncertain. Site-specific approaches are usually needed, involving analysis for more specific chemical constituents. Many of the chemicals are petroleum hydrocarbons often classified as long-chain paraffins, which show relatively modest water solubility or potential to migrate offsite or into groundwater. While not viewed as a major data need, additional studies on the environmental fate of the various chemicals in this category of hydraulic fluids would be useful for assessing potential human exposure near hazardous waste sites.

Organophosphate Ester Hydraulic Fluids. Information is available on many of the major components of organophosphate ester hydraulic fluids, particularly on their aerobic biodegradation, monitoring, and environmental partitioning. Little research can be identified dealing with the actual multi-component mixtures typical of most hydraulic fluid products. There is also little information on some of the degradation products of organophosphate esters, such as diesters of phosphoric acid. Given the concerns over the toxicity of the organophosphate ester class of chemicals, further research for this category of hydraulic fluids is warranted. The development of this information will allow an assessment of the environmental transport, distribution, transformation, and degradation processes and provide a better understanding of how these processes affect environmental contamination. Given the tendency of organophosphate ester hydraulic fluids to partition to soils and sediments, research should be focussed on these media. More research is needed on the reactive importance of chemical degradation processes such as hydrolysis in relation to the potential for biodegradation by some strains of bacteria (Pickard et al. 1974).

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Bioavailability from Environmental Media.

Mineral Oil Hydraulic Fluids and Polyalphaolefin Hydraulic Fluids. No literature was identified dealing with the bioavailability of chemicals in this category of hydraulic fluids. Because of this wide variation and the lack of any information in mammalian species, it is difficult to estimate bioavailability to humans. Additional research on the bioavailability of this category of hydraulic fluids would be valuable but may not be as high a priority as research on bioavailability issues for the phosphate ester-based hydraulic fluids.

Organophosphate Ester Hydraulic Fluids. Very little is known about the bioavailability of organophosphorus esters. In fish, organophosphate esters appear to be more bioavailable when sediments are not present (Huckins et al. 1991), but chironomids appear to be able to bioaccumulate organophosphate esters from the sediments (Muir et al. 1983b, 1985). Because of this wide variation and the lack of any information in mammalian species, it is difficult to estimate bioavailability to humans. Development of bioavailability information in mammalian species will allow a better understanding of this complex process. Given the concerns over the toxicity of this class of hydraulic fluids, further research on this topic would be useful.

Food Chain Bioaccumulation.

Mineral Oil Hydraulic Fluids and Polyalphaolefin Hydraulic Fluids. While very little information dealing explicitly with the food chain bioaccumulation of this category of hydraulic fluids is available, the principle petroleum hydrocarbon constituents do not appear to have a significant tendency for bioconcentration, bioaccumulation, or biomagnification. There do not appear to be any major research needs on this topic for this class of hydraulic fluids.

Organophosphate Ester Hydraulic Fluids. Very little information on the food chain bioaccumulation of organophosphate ester hydraulic fluids is available. It is known that some organisms bioconcentrate components of organophosphate ester hydraulic fluids (values are 133-2,807 for rainbow trout and 596-928 for fathead minnows) (Lombardo and Egry 1979; Mayer et al. 1981; Muir et al. 1983a; Veith et al. 1979). Given the concerns over the toxicity of this class of hydraulic fluids, further research on this topic would be useful.

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Exposure Levels in Environmental Media. Reliable monitoring data for the levels of all types of hydraulic fluids in contaminated media at hazardous waste sites are needed so that the information obtained on levels of these hydraulic fluids in the environment can be used in combination with the known body burden of these hydraulic fluids to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites.

Mineral Oil Hydraulic Fluids and Polyalphaolefin Hydraulic Fluids. Very limited information is available concerning levels of these hydraulic fluids in environmental media. The only available study described concentrations at a spill site (Abdul et al. 1990). No other reports of mineral oil hydraulic fluid exposure levels in environmental media were found in the available literature. At NPL sites, it becomes difficult to decide which original products are associated with documentation of specific site contaminants. General research dealing with assessment techniques relevant to complex petroleum hydrocarbon mixtures would be helpful in deciding how to approach the environmental media exposure issues.

Organophosphate Ester Hydraulic Fluids. A large amount of monitoring data is available that describes the presence of many of the components of organophosphate ester hydraulic fluids in the environment (Deleon et al. 1986; EPA 1978, 1979a; FMC 1977c, 1979, 1980; Konasewich et al. 1978; Mayer et al. 1981; Monsanto 1981; Sheldon and Hites 1978, 1979; Strachan 1974; Weber and Ernst 1983). Additional research on this topic for the organophosphate ester hydraulic fluids is not a major data need.

Exposure Levels in Humans.

Mineral Oil Hydraulic Fluids and Polyalphaolefin Hydraulic Fluids. Very little current workplace monitoring data is available for this class of hydraulic fluids. The only studies that are available discuss leakage (Perl et al. 1985) and alkane concentrations in an office building (Weschler et al. 1990). These hydraulic fluids are used in virtually every manufacturing and heavy industrial site as well as in most cars, so potentially exposed populations are very large. More data that better define the concentrations of mineral oil hydraulic fluid components in the workplace and in the vicinity of major industrial plants that-use hydraulic fluids would allow an assessment of the exposure levels of these populations. Some difficulty may be encountered in isolating hydrocarbons that result from use of mineral oil hydraulic fluid versus use of other mineral-oil-based products such as lubricants. Research efforts should be focused on populations where higher exposures are expected. Targeted research efforts on workplace exposure could be of great value to

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document exposure risks resulting directly from hydraulic fluids as opposed to exposure to products (e.g., lubricants) that contain similar chemical components.

Organophosphate Ester Hydraulic Fluids. Very little workplace monitoring data is available for organophosphate ester hydraulic fluids. The available study reports workplace air concentrations in an airport hangar (Labour Canada 1990). Since organophosphate ester hydraulic fluids are used in many manufacturing and heavy industrial sites and in aircraft (both military and civilian), potentially exposed populations are large. More data that better define the concentrations of organophosphate ester hydraulic fluid components would allow an assessment of the exposure levels of these populations. Some difficulty may be encountered in isolating organophosphate esters that result from hydraulic fluid use versus use of other organophosphate ester-containing products such as lubricants.

This information is necessary for assessing the need to conduct health studies on these populations.

Exposure Registries. No exposure registries for hydraulic fluids were located. This substance is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry. The substance 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 exposure to this substance.

5.7.2 Ongoing Studies

Mineral Oil Hydraulic Fluids. No information concerning ongoing studies on mineral oil or water-in-oil emulsion hydraulic fluids was located in the available literature.

Organophosphate Ester Hydraulic Fluids. The EPA has published a proposed test rule (EPA 992b) for testing aryl phosphate base stocks. The proposed tests include: 120-day post-hatch trout, chronic exposure neurotoxicity in the hen, two-generation reproduction and fertility effects, anaerobic biodegradation, chronic *Daphnia magna*, subchronic mammalian toxicity, aerobic biodegradation, microcosm ecosystem, and developmental toxicity. Since this proposed rule was published in January 1992, the comment period has closed, and EPA is considering what stocks to test, what tests to proceed with, and how to implement any testing program. As of early 1997, no final test rule had been published.

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Polyalphaolefin Hydraulic Fluids. No information concerning ongoing studies on polyalphaolefin hydraulic fluids was located in the available literature.