

## **5. POTENTIAL FOR HUMAN EXPOSURE**

### **5.1 OVERVIEW**

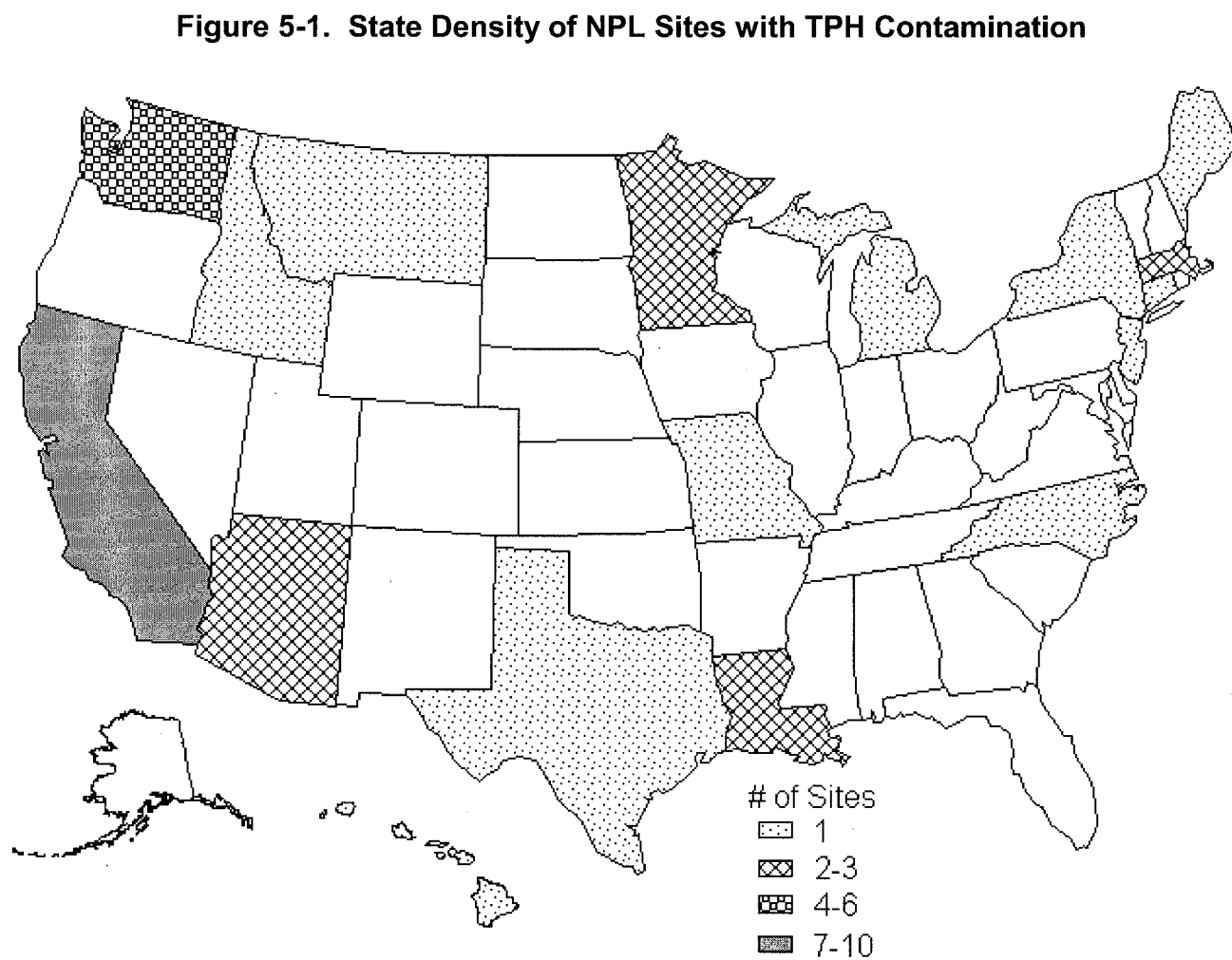
Petroleum products are an integral part of our modern lives. It is nearly impossible to avoid exposure to hydrocarbons from petroleum products, whether it is from gasoline fumes at the pump, spilled crankcase oil on asphalt, solvents used at home or work, or pesticide applications that use petroleum products as carriers. There are concerns with both short-term (accidents) and long-term exposures to petroleum hydrocarbons (e.g., contaminated drinking water). Gross measures of Total Petroleum Hydrocarbons (TPH) in soil or water are not particularly valuable for assessing either the potential for exposure to TPH or the impacts of such exposure on public health. This chapter addresses questions related to the first point: what are the levels of contamination in the environment, what happens to petroleum hydrocarbons in the environment, and what is the likelihood that individuals or populations will be exposed to petroleum hydrocarbons at levels thought to be of concern?

Petroleum products are released to the environment through accidents, as managed releases, or as unintended by-products of industrial, commercial or private actions. An understanding of the changes that occur over time in the composition of petroleum hydrocarbons found in soil, water, or air is extremely important in addressing public health issues for TPH. The TPH Criteria Working Group (TPHCWG 1997b) has defined its TPH fractions by the mobility of constituents in order to address this question of predicting risks associated with TPH contamination.

The following sections present an overview of releases to the environment (5.2), fate and transport (5.3), and levels found in the environment (5.4).

### **5.2 RELEASES TO THE ENVIRONMENT**

TPH has been identified in 34 of the 1,519 current or former EPA National Priorities List (NPL) hazardous waste sites (ATSDR 1998a). Components of TPH are common environmental contaminants in all media and are likely contaminants at many NPL sites. However, the number of sites evaluated for TPH and TPH components is not known. The frequency of the TPH reported sites within the United States can be seen in Figure 5- 1.



Source: HazDat 1999

The number of NPL sites reporting TPH contamination is a small subset of those contaminated with petroleum hydrocarbons.

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Raw petroleum and refined petroleum products used as fuels or lubricants are generally excluded at the national level from the cradle-to-grave record-keeping associated with recognized toxics such as heavy metals or chlorinated solvents. With an eye to the availability of petroleum as a source of energy, petroleum production is tracked by the federal government as well as industry trade associations. Statistics are available for wellhead production as well as for production of major bulk fuel types from domestic refineries. These primary production statistics have been summarized in Chapter 4.

Once processed into products such as motor gasoline and fuel oil, most of the petroleum is burned in engines or boilers to provide energy for transportation, space heating, or electricity. In these combustion processes, the petroleum fuel is oxidized. Because of incomplete oxidation, small amounts of hydrocarbon emissions result. These emissions often contain much larger percentages of combustion by-products such as polycyclic aromatic hydrocarbons (PAHs) than the initial petroleum products. Incomplete combustion and heat also alter the composition of crank case oils and lubricants.

Emissions statistics are usually lacking for TPH or most TPH fractions since there is no record-keeping associated with smaller internal combustion engines used in cars and trucks or fuel oil boilers for individual buildings or homes. These individual uses account for the majority of petroleum product use. These releases, mostly to the atmosphere from incomplete combustion, however, are generally small compared to a variety of other releases connected with spills or uncontrollable losses during storage, transport, or fueling operations.

The movement of raw petroleum to automobile fuel tanks or fuel oil boilers is part of a complex bulk product distribution and storage system, providing many opportunities for accidents, spills, leaks, and losses from simple volatilization. Consistent national statistics are lacking for many stages in the overall oil distribution and storage system. The main exceptions involve larger leaks and spills, especially spills in coastal areas or on larger navigable rivers.

Data for the period from 1984 through 1993 (API 1996) show that most data reported to the U.S. Coast Guard occurred in inland bodies of water: rivers, lakes, and points on bays or estuaries. Spills from large ocean-going tankers and large spills in general (more than 1,000 gallons) are relatively

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infrequent, never more than 5% of the total number of reported spills in a year. The average number of spills during the 1984-93 period was just under 6,000 spills. The numbers in any given year can vary enormously, with a maximum of just under 9,600 spills reported in 1991.

In terms of the amounts of oil estimated from spills, large spills, although rare, can dominate the annual totals. For instance, of about 14,000,000 total estimated gallons of oil spilled to U.S. waters in 1989, 10.8 million gallons resulted from the Exxon Valdez catastrophe in the coastal waters of Alaska. One or two large tanker spills in the course of a decade can make it very hard to draw conclusions on trends. The average amount of oil spilled in the 5-year period from 1984 to 1988 was 6.3 million gallons per year, compared to 5.6 million gallons spilled from 1989 to 1993. With eventual implementation of double-hull requirements for large tankers required in the Oil Pollution Act of 1990, the releases from tankers should be greatly curtailed.

Within the broad reporting categories of vessels (tankers and barges) and facilities (pipelines, tanks, batteries, and other onshore facilities) in the period 1984-1993, numbers of reported spill incidents were roughly equivalent: 42,000 incidents from vessels and 38,000 from facilities. Over this period, the vessels spilled a much larger cumulative amount of oil: 45 million gallons from vessels versus 15 million gallons for facilities. Major incidents can dominate these totals. Two vessel spills account for around one-third of the vessel totals.

Most spills involve either crude oil or bulk fuels (distillates) such as fuel oils. Four tables (adapted from API 1996) help summarize annual figures on oil spills to coastal and inland waters of the United States. Table 5-1 shows statistics on the number of spills broken out by size categories, where the prevalence of very small releases is obvious. Table 5-2 summarizes releases from vessels, and Table 5-3 summarizes releases from facilities. Table 5-4 summarizes spills according to the type of petroleum product involved.

At the national level, virtually the only other regulatory program that provides broad-based statistics on petroleum product releases to the environment is EPA's (leaking) Underground Storage Tank (UST) Program. In 1994, there were over a million underground storage tanks on more than 300,000 identified UST sites; about 91% of these involve tanks at gasoline stations, truck stops, vehicle repair shops, or convenience stores selling gasoline or diesel fuel (EPA 1998c). There were at least

**Table 5-1. Total Number of Oil Spills by Size: 1984–1996**

Year	Under 10 Gallons	10–999 Gallons	1,000–9,999 Gallons	10,000–99,999 Gallons	More than 100,000 Gallons	Total
1984	5,446	3,273	366	74	16	9,175
1985	4,210	2,571	311	52	9	7,153
1986	3,737	2,285	128	25	11	6,186
1987	3,544	2,250	128	23	8	5,953
1988	3,626	2,238	125	29	11	6,029
1989	5,024	2,580	136	37	7	7,784
1990	6,480	2,720	164	43	11	9,418
1991	6,791	2,620	138	25	3	9,577
1992	6,322	2,556	105	22	3	9,008
1993	6,897	2,316	120	16	3	9,352
1994	6,659	2,376	144	21	8	9,208
1995	6,648	2,330	75	14	2	9,069
1996	6,182	1,843	105	16	5	8,151
avg 1992–1996	6,542	2,284	110	18	4	8,958

Source: Adapted from API 1998b

Table 5-2. Total Number of Oil Spill from Vessels: 1984–1996

Year	Under 10 Gallons	10–999 Gallons	1,000–9,999 Gallons	10,000–99,999 Gallons	More than 100,000 Gallons	Total
1984	1,333	1,079	78	21	13	2,524
1985	1,178	952	59	13	7	2,209
1986	1,661	1,260	74	15	8	3,018
1987	1,723	1,228	62	13	7	3,033
1988	1,896	1,299	57	23	7	3,282
1989	2,197	1,440	66	25	5	3,733
1990	2,576	1,533	92	28	7	4,236
1991	2,689	1,446	70	12	2	4,219
1992	3,910	1,687	49	6	1	5,653
1993	4,098	1,520	67	8	2	5,695
1994	3,759	1,545	68	11	2	5,385
1995	3,932	1,530	44	11	2	5,519
1996	3,722	1,201	60	10	3	4,996
avg 1992–1996	3,884	1,497	58	9	2	5,450

Source: Adapted from API 1998b

**Table 5-3. Total Number of Oil Spill from Facilities: 1984–1996**

Year	Under 10 Gallons	10–999 Gallons	1,000–9,999 Gallons	10,000–99,999 Gallons	More than 100,000 Gallons	Total
1984	4,113	2,194	288	53	3	6,651
1985	3,032	1,619	252	39	2	4,944
1986	2,076	1,025	54	10	3	3,168
1987	1,821	1,022	66	10	1	2,920
1988	1,730	939	68	6	4	2,747
1989	2,827	1,140	70	12	2	4,051
1990	3,904	1,187	72	15	4	5,182
1991	4,102	1,174	68	13	1	5,358
1992	2,412	869	56	16	2	3,355
1993	2,799	796	53	8	1	3,657
1994	2,900	831	76	10	6	3,823
1995	2,716	800	31	3	0	3,550
1996	2,460	642	45	6	2	3,155
avg 1992-1996	2,657	788	52	9	2	3,508

Source: Adapted from API 1998b

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**Table 5-4. Nature of Oil Spill by Material or Product: 1984–1996<sup>a</sup>**  
**(Volume in Thousands of Gallons)**

Material	Number of spills 1984–1993 <sup>a</sup> ( <i>avg annual</i> )	Number of Spills 1996	Volume of spills 1984–1993 <sup>a</sup> ( <i>avg annual</i> )	Volume of spills 1996
Residuals	3,478 (348)	132	6,135 (614)	276
Distillates	27,035 (2,704)	2,403	12,776 (1,277)	2,256
Crude oils	15,973 (1,597)	1,450	30,364 (3,036)	195
Lubricants	7,563 (756)	634	1,784 (178)	24
Light ends	104 (10)	–	124 (12)	–
Miscellaneous	11,925 (1,193)	–	2,308 (231)	–
Unknown	4,728 (473)	–	239 (24)	–
Gasoline	5,858 (586)	454	3,583 (358)	291
Asphalt	489 (49)	24	414 (41)	20
Jet fuel	1,011 (101)	65	1,111 (111)	18
Bilge oil	311 (31)	177	6 (0.6)	2
Benzene and related aromatics	88 (9)	11	148 (15)	8
Naphthas	338 (34)	10	268 (27)	3
Kerosene	478 (48)	18	542 (54)	1
Liquified natural gas	29 (3)	–	0	–
Waxes	18 (2)	–	4 (0.4)	–
Liquified petroleum gas	37 (4)	–	15 (1.5)	–
All other		2,773		114
<b>Total</b>	<b>79,463 (7,946)</b>	<b>8,151</b>	<b>59,820 (5,982)</b>	<b>3,208</b>

<sup>a</sup> Data not available for 1994 and 1995

Source: Adapted from API 1998b



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119,000 confirmed instances of underground releases of gasoline or similar petroleum bulk fuels to soils or groundwater, with the total number of sites needing remediation likely to climb to over 176,000 by the turn of the century (EPA 1994a). While tests to confirm contamination may involve TPH or tests for surrogates of specific chemicals such as benzene, the UST program does not attempt to make detailed estimates of releases to environmental media.

Since many releases of petroleum to environmental media involve unintentional leakage or spillage, it can be helpful to present some rough estimates of release from various categories of activities or components within the overall petroleum production and distribution system. Results assembled from various sources in a study by Doyle (1994) are summarized in Table 5-5. While different estimation techniques could alter these leakage values, the major components of the oil production and distribution system include: leaking (abandoned) oil wells, large aboveground storage tanks, leaks from gasoline stations, tank bottoms and refinery residuals disposal, used motor oil, and evaporative losses.

Doyle (1994) estimates the total amount of leakage or spillage related to petroleum product production, processing, and distribution to end users at around 134 million barrels per year (see Table 5-5); different estimation approaches could lead to slightly different total figures. For instance, total U.S. refinery output in 1993 was around 2,608 million gallons (PennWell 1994); total consumption of motor gasoline during 1992 was around 5,762 million barrels (PennWell 1994). The levels of spillage or leakage resulting in releases to the environment amount to about 2.3% of total refinery output and around 5% of total gasoline consumed; conversely, about 95% of the original amounts petroleum products are completely consumed, generally in combustion processes to heat homes or power cars, trucks, planes, boats, and trains.

Recurrent spills or a long history of disposal at specific sites can lead to concerns. Oil dumped onto soils can saturate the soil matrix (see Section 5.3). This type of very concentrated contamination can be virtually impossible to eliminate without excavating and removing all the soil materials.

If TPH is introduced at any depth within the soil matrix, as in the case of leaks from underground storage tanks, natural weather and biodegradation processes are rendered less effective and the chances are increased that some of the TPH fractions may contaminate groundwater. Since many

**Table 5-5. Estimated Releases From Components of the Oil System  
(Annual Estimates in Millions of Barrels per Year)**

Type of release	Size of release	Major media impacted	Description of category
Oilfield spills	1.050 (<1%)	Soil Surface water Groundwater	Producing wells and tank batteries.
Leaking oil wells	3.650 (2.7%)	Soil Surface water Groundwater	Older "abandoned" wells never capped; up to 1.2 million such wells in the United States.
Oil in waste pits or produced water	1.200 (<1%)	Soil Groundwater	Buried or land applied wastes from producing wells or exploration activities.
Aboveground tanks	63.875 (47.4%)	Soil, Air, Groundwater	Usually larger tank batteries, often part of interstate pipeline systems.
Existing underground plumes	1.200 (<1%)	Groundwater Soil	Tank farms, transshipment terminals, and refineries with large amounts of "free product" beneath the facilities. At least 356 facilities currently pump from the largest plumes.
Pipelines	0.714 (<1%)	Surface water Soil	Larger interstate pipelines and low pressure gathering systems from smaller tank batteries.
Leaks from gas stations	5.200 (3.9%)	Soil Groundwater	At least 25% of the nation's filling stations may face remediation under the UST program.
Tank bottoms & refinery waste	24.200 (17.9%)	Soil	Heavier residuals and sludges from refineries.
Used motor oil	14.000 (10.4%)	Water Soil	The U.S. generates about 1.4 billion gallons of used motor oil per year. Less than half is re-refined. Much "home fix-it" oil is not disposed of properly.
Oil spills in U.S. waters	1.095 (<1%)	Surface water	Tankers, barge, and pipeline accidents, mostly during vessel loading or unloading operations.
Oil & grease discharge	0.090 (<1%)	Surface water	Mostly from offshore drilling in near coastal waters.
Operational discharges from tankers	0.178 (<1%)	Surface water	Discharge of cargo and bilge oil in near coastal waters.
Evaporative losses	18.428 (13.7%)	Air	Transfers at refineries or tankers, losses at storage facilities, and during vehicle fueling. Up to 18 grams of hydrocarbons vented to air for each gallon of gasoline used.
<b>Total</b>	<b>134.880</b>		

Source: Adapted from Doyle 1994

TPH components have densities less than or close to that of water, these lighter nonaqueous phase liquids (LNAPLs) generally pose less potential for groundwater pollution than most chlorinated solvents (e.g., PCBs or TCE) that are denser than water (denser nonaqueous phase liquids [DNAPLs]). The nonaqueous phase liquid refers to liquids that are immiscible in water. Still, there are risks for shallow groundwater supplies, which may be used for private wells for drinking water purposes.

For surface water, the relatively low density of many petroleum fractions can pose some major short-term concerns, especially for fish and wildlife. Many petroleum fractions float in water and form thin surface films (Jordan and Payne 1980; Mackay 1984). Gasoline, diesel, or other common fuel oils when spilled to water quickly spread out into a film 0.1 millimeter or less in thickness. This means that a very small amount of oil can create a film over a very large area of water surface. While natural physical and biological weathering processes will dissipate or degrade such oil slicks in time frames ranging from days to a few weeks, there is considerable short-term opportunity for damage to water fowl, aquatic mammals, fish, and other aquatic organisms. For inland waters, large oil spills may force shutdowns in surface water withdrawals for public drinking water supplies until the surface slicks have dissipated (Clark et al. 1990). Where the spilled petroleum washes up onto beaches or shorelines, there may be short-term damage to fish and wildlife as well as impacts to recreational use of shoreline or riparian areas for human swimming or fishing.

Some heavier petroleum fractions, including the chemicals called PAHs found in motor oils or as byproducts of combustion, show neutral buoyancy or may be heavier than water. Such components can accumulate in substrates. This can lead to stresses for benthic organisms, shellfish, or bottom feeding fish. PAHs or “tarballs” formed when lighter oil fractions combine with suspended sediment or algae can have a serious impact on a water body’s use for commercial fishing or shellfishing and its value for recreational swimming or sports fishing.

In addition to releases from the various components or activities that make up the production and distribution system for petroleum products (the oil system), many older waste sites show TPH-related site contamination. Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) site descriptions often mention petroleum, oil and grease, or petroleum, oil, and lubricants (POL) as present at a former waste disposal site. An example is given below for a waste oil recycling site, where TPH-type chemicals were obviously a common site contaminant. The CERCLA clean-up actions, however, focus on a range of specific hazardous or toxic chemicals. Some of the specific chemicals (e.g., toluene) would show up in a TPH test, but the chlorinated solvents and metals do not.

Since a site cannot be prioritized for CERCLA attention if the only problem involves TPH site contamination, CERCLA actions are often triggered by the presence of other site contaminants that can clearly be ranked as hazardous or toxic. The long-term clean-up actions may entail remediation steps that reduce or eliminate the TPH concerns, but these actions are secondary results of the cleanup activities.

This oil exemption aspect of CERCLA introduces complications when trying to present summary data on the distribution of NPL sites showing TPH site contamination. The ATSDR HazDat database contains only 34 records dealing explicitly with TPH at current or former NPL sites (ATSDR 1998a).

While CERCLA deals with former waste disposal sites, the RCRA program handles active waste disposal facilities. Many waste facilities still in use have older sites (management units) within them that may need corrective actions similar to those encountered at CERCLA NPL sites. At least 5,100 RCRA hazardous waste treatment, storage, and disposal facilities (TSDFs) may need some corrective actions before they can be shut down (EPA 1994b). While there are no readily available statistics, many of these RCRA facilities needing corrective actions also contain waste oils (EPA 1994b). As with CERCLA, RCRA works with what amounts to a hazardous waste exclusion clause for ordinary petroleum products. Most clean-up efforts, therefore, focus on legally defined toxics and hazardous materials as the main line of attack in site remediation, with the expectation that these measures will also help ameliorate any TPH-related concerns.

### **5.3 FATE AND TRANSPORT**

#### **5.3.1 Overview**

Chemical analysis for all individual compounds in a petroleum bulk product released to the environment is generally unrealistic due to the complexity of these mixtures and the laboratory expense. Determining the chemical composition of a petroleum release is further complicated by hydrodynamic, abiotic, and biotic processes that act on the release to change the chemical character. The longer the release is exposed to the environment, the greater the change in chemical character and the harder it is to obtain accurate analytical results reflecting the identity of the release. After extensive weathering, detailed knowledge of the original bulk product is often less valuable than current site-specific information on a more focused set of hydrocarbon components, for example TPH fractions.

Health assessment efforts are frequently frustrated by three primary problems: (1) the inability to identify and quantify the individual compounds released to the environment as a consequence of a petroleum spill; (2) the lack of information characterizing the fate of the individual compounds in petroleum mixtures; and (3) the lack of specific health guidance values for the majority of chemicals present in petroleum products. To define the public health implications associated with exposure to petroleum hydrocarbons, it is necessary to have a basic understanding of petroleum properties, compositions, and the physical, chemical, biological, and toxicological properties of the compounds most often identified as the key chemicals of concern.

### **5.3.2 Fate and Transport Processes**

This section describes important chemical, physical, and biological processes that affect the behavior of hydrocarbon compounds in the environment. This information may be used to identify the environmental media that are likely to be affected by a release and to predict the potential for subsequent human exposure.

#### **5.3.2.1 Bulk Oil Migration**

Petroleum products released to the environment migrate through soil via two general pathways: (1) as bulk oil flow infiltrating the soil under the forces of gravity and capillary action, and (2) as individual compounds separating from the bulk petroleum mixture and dissolving in air or water. When bulk oil flow occurs, it results in little or no separation of the individual compounds from the product mixture and the infiltration rate is usually fast relative to the dissolution rate (Eastcott et al. 1989). Many compounds that are insoluble and immobile in water are soluble in bulk oil and will migrate along with the bulk oil flow. Factors affecting the rate of bulk oil infiltration include soil moisture content, vegetation, terrain, climate, rate of release (e.g., catastrophic versus slow leakage), soil particle size (e.g., sand versus clay), and oil viscosity (e.g., gasoline versus motor oil).

As bulk oil migrates through the soil column, a small amount of the product mass is retained by soil particles. The bulk product retained by the soil particles is known as “residual saturation.”

Depending upon the persistence of the bulk oil, residual saturation can potentially reside in the soil for years (Dragun 1988). Residual saturation is important as it determines the degree of soil contamination and can act as a continuing source of contamination for individual compounds to separate from the bulk product and migrate independently in air or groundwater (Bauman 1988). If

the release is persistent in the environment, there can be impacts to extensive areas as the individual compounds continue to separate and migrate away from the spill area via air or groundwater.

When the amount of product released to the environment is small relative to the volume of available soil, all of the product is converted to residual saturation and downward migration of the bulk product usually ceases prior to affecting groundwater resources. Adverse impacts to groundwater may still occur if rain water infiltrates through soil containing residual saturation and initiates the downward migration of individual compounds.

When the amount of product released is large relative to the volume of available soil, the downward migration of bulk product ceases as water-saturated pore spaces are encountered. If the density of the bulk product is less than that of water, the product tends to “float” along the interface between the water saturated and unsaturated zones and spread horizontally in a pancake-like layer, usually in the direction of groundwater flow. Almost all motor and heating oils are less dense than water (Knox 1993; Mackay 1988) and are referred to as LNAPLs.

If the density of the bulk product is greater than that of water, the product will continue to migrate downward through the water table aquifer under the continued influence of gravity. Downward migration ceases when the product is converted to residual saturation or when an impermeable surface is encountered. Polychlorinated biphenyls and other chlorinated organic solvents are usually denser than water and are characterized as DNAPLs.

In reality, bulk oil flow is affected by numerous product-specific and site-specific factors. As a consequence, product distribution in the subsurface can be quite complex.

### 5.3.2.2 Compound Migration

As the bulk product migrates through the soil column, individual compounds may separate from the mixture and migrate independently. Chemical transport properties such as volatility, solubility, and sorption potential are often used to evaluate and predict which compounds will likely separate from the mixture.

**Volatility.** Volatility is defined as the propensity of a chemical to partition to air and migrate as a vapor. It is primarily a function of the vapor pressure of the compound. Vapor pressure is defined as the pressure of a chemical exerted by its vapor when in equilibrium with the solid or liquid form of

that chemical. For example, if a chemical in a liquid form is placed in a closed container, molecules of the chemical that possess relatively high kinetic energy will migrate to the surface of the liquid and evaporate into the air space in the container.

Since petroleum products are complex mixtures of hundreds of compounds, the compounds characterized by relatively high vapor pressures tend to volatilize and enter the vapor phase. The exact composition of these vapors depends on the composition of the original product. Using gasoline as an example, compounds such as butane, propane, benzene, toluene, ethylbenzene and xylene are preferentially volatilized (Bauman 1988). Because volatility represents transfer of the compound from the product or liquid phase to the air phase, it is expected that the concentration of that compound in the product or liquid phase will decrease as the concentration in the air phase increases.

In general, compounds having a vapor pressure in excess of  $10^{-2}$  mm Hg are more likely to be present in the air phase than in the liquid phase. Compounds characterized by vapor pressures less than  $10^{-7}$  mm Hg are more likely to be associated with the liquid phase. Compounds possessing vapor pressures that are less than  $10^{-2}$  mm Hg, but greater than  $10^{-7}$  mm Hg, will have a tendency to exist in both the air and the liquid phases (Knox 1993).

Although volatility is a function of vapor pressure, environmental factors affect the rate of volatilization. For example, high summer temperatures enhance volatilization, particularly when soils begin to dry out. The rate of volatilization is also a function of air and soil temperature, humidity, wind speed, soil type, moisture content, oil composition, solar radiation, and thickness of the oil layer. Volatilization of benzene, toluene, ethylbenzene, and xylene from gasoline-contaminated soils tends to increase with decreasing moisture content (Frankenberger 1992). Bossert and Bartha (1986) indicated that *n*-alkanes greater than  $C_{18}$  exhibit no substantial volatilization at ambient temperatures; however, lighter fractions ( $<C_{18}$ ) are subject to volatilization.

The propensity for a compound to volatilize from an aqueous phase can be grossly estimated using Henry's law, which relates vapor pressure, solubility, and molecular weight. Henry's law constant can be estimated using these three chemical-specific parameters or it can be measured on a compound-by-compound basis in the laboratory. Henry's law constant is frequently used to assess the environmental fate of organic compounds in the subsurface.

**Solubility.** Solubility is one of the key factors in determining compound behavior, and thus the impact, of a chemical in the environment. Solubility is expressed in terms of the number of milli-

grams of pure chemical that can be dissolved in one liter of water under standard conditions of 25 °C and one atmosphere of pressure. The solubility of an organic compound determines its propensity to dissolve into water. The greater the solubility, the greater the likelihood that the chemical will dissolve into infiltrating rainwater or groundwater and migrate away from the release area.

Solubility generally decreases with increasing molecular weight of the hydrocarbon compounds. For compounds having similar molecular weights, the aromatic hydrocarbons are more water soluble and mobile in water than the aliphatic hydrocarbons (ASTM 1995) and branched aliphatics are less water-soluble than straight-chained aliphatics. Coleman et al. (1984) determined that the compounds most likely to be measured in water in contact with gasoline, kerosene, and fuel oil #2 were the light-fraction, aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes. They found that although the aromatic compounds in these three fuels may comprise as much as 50% by weight, aromatic compounds in the C<sub>6</sub>-C<sub>13</sub>, range made up approximately 95% of the compounds dissolved in water. This correlates well with studies showing an enrichment of light-fraction hydrocarbons in the water phase and a depletion in the fuel phase.

It is important to note that the partitioning behavior of organic compounds is affected by the presence of other hydrocarbons in the subsurface. The maximum dissolved concentrations achieved in the subsurface are always less than the concentration of any pure compound, when it is present as one of many constituents of a petroleum product (ASTM 1995). For example, the solubility of pure benzene in water is given as 1,780 mg/L, but the maximum calculated concentration in an aquifer immediately beneath a gasoline release has been estimated to be about 62 mg/L (Daugherty 1991).

**Organic Carbon-Water Partition Coefficient.** The organic carbon-water partition coefficient ( $K_{oc}$ ) describes the propensity for a organic compound to partition between water and organic carbon in the soil. Chemical mobility can be determined based on the likelihood of a chemical to partition more strongly to either the organic carbon in the substrate or the water. If the chemical is strongly associated with the substrate (i.e., sorbed), the chemical is relatively immobile and will not be leached or transported great distances from the area of the release. In contrast, if the chemical is weakly sorbed to the substrate, the chemical has the potential to be transported greater distances and greater chance to contact human receptors.

The degree of sorption not only affects the mobility of the compound, it can also affect other transport and transformation reactions. For example, volatilization and biodegradation rates are directly dependent upon the extent of partitioning (Dragun 1988). A compound that is strongly



sorbed to the organic carbon in the substrate is less available and less likely to be volatilized or biodegraded.

A mobility classification scheme based on the  $K_{oc}$  indicates that compounds having  $K_{oc}$  values <50 L/kg, 50-150 L/kg, and 150-500 L/kg are considered to be very mobile, mobile, and intermediate in mobility, respectively (Dragun 1988). Using this scheme, benzene ( $K_{oc} = 60$  L/kg) is classified as mobile; whereas toluene, ethylbenzene, and total xylenes ( $K_{oc} = 182$  L/kg,  $K_{oc} = 363$  L/kg, and  $K_{oc} \cong 400$  L/kg, respectively) are classified as having intermediate immobility.

In summary, lighter petroleum products such as gasoline contain constituents with higher water solubility and volatility and lower sorption potential than heavier petroleum products such as fuel oil. Data compiled from gasoline spills and laboratory studies indicate that these light-fraction hydrocarbons tend to migrate readily through soil, potentially threatening or affecting groundwater supplies. In contrast, petroleum products with heavier molecular weight constituents, such as fuel oil, are generally more persistent in soils, due to their relatively low water solubility and volatility and high sorption capacity (Stelljes and Watkin 1991).

### 5.3.2.3 Biodegradation

Indigenous microbes found in many natural settings (e.g., soils, groundwater, ponds) have been shown to be capable of degrading organic compounds. Biodegradation occurs as microbes use organic compounds as a source of energy. Unlike other fate processes that disperse contaminants in the environment, biodegradation can eliminate the contaminants without transferring them across media. The final products of microbial degradation are carbon dioxide, water, and microbial biomass.

The rate of hydrocarbon degradation depends on the chemical composition of the product released to the environment as well as site-specific environmental factors. Generally the straight chain hydrocarbons and the aromatics are degraded more readily than the highly branched aliphatic compounds (Havlicek 1988). The *n*-alkanes, *n*-alkyl aromatics, and the aromatics in the  $C_{10}$ - $C_{22}$  range are the most readily biodegradable; *n*-alkanes, *n*-alkyl aromatics, and aromatics in the  $C_5$ - $C_9$  range are biodegradable at low concentrations by some microorganisms, but are generally preferentially removed by volatilization and thus are unavailable in most environments; *n*-alkanes in the  $C_1$ - $C_4$  ranges are biodegradable only by a narrow range of specialized hydrocarbon degraders; and *n*-alkanes, *n*-alkyl aromatics, and aromatics above  $C_{22}$  are generally not available to degrading microorganisms. Hydrocarbons with condensed ring structures, such as PAHs with four or more

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rings, have been shown to be relatively resistant to biodegradation. PAHs with only 2 or 3 rings (e.g., naphthalene, anthracene) are more easily biodegraded (Park et al. 1990).

A large proportion of the water-soluble fraction of the petroleum product may be degraded as the compounds go into solution. As a result, the remaining product may become enriched in the alicyclics, the highly branched aliphatics, and PAHs with many fused rings.

Environmental factors such as oxygen content, pH, moisture content, temperature, nutrient concentrations, and the microbiota also affect the rate of biodegradation. In almost all cases, the presence of oxygen is essential for effective biodegradation of oil. Anaerobic decomposition of petroleum hydrocarbons leads to extremely low rates of degradation (Frankenberger 1992). The ideal pH range to promote biodegradation is close to neutral (6-8). For most species, the optimal pH is slightly alkaline, that is, greater than 7 (Dragun 1988). The moisture content of the contaminated soil will affect biodegradation of oils due to dissolution of the residual compounds, dispersive actions, and the need for microbial metabolism to sustain high activity. The moisture content in soil affects microbial locomotion, solute diffusion, substrate supply, and the removal of metabolic by-products. Excessive moisture will limit the gaseous supply of oxygen for enhanced decomposition of petroleum hydrocarbons. Most studies indicate that optimum moisture content is within 50-70% of the water holding capacity (Frankenberger 1992).

All biological transformations are affected by temperature. Generally, as the temperature increases, biological activity tends to increase up to a temperature where enzyme denaturation occurs. The presence of oil should increase soil temperature, particularly at the surface. The darker color increases the heat capacity by adsorbing more radiation. The optimal temperature for biodegradation to occur ranges from 18 °C to 30 °C. Minimum rates would be expected at 5 °C or lower (Frankenberger 1992).

There are at least 11 essential macronutrient and micronutrient elements that must be present in the soil in proper amounts, forms, and ratios to sustain microbe growth (Dragun 1988). These 11 elements are nitrogen, phosphorus, potassium, sodium, sulfur, calcium, magnesium, iron, manganese, zinc, and copper. Nitrogen is usually the main limiting nutrient governing the rate of decomposition of petroleum hydrocarbons. However, small amounts of phosphorus fertilizers may also be necessary to stimulate biodegradation (Mills and Frankenberger 1994).

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Biodegradation rates in soils are also affected by the volume of product released to the environment. At concentrations of 1-0.5% of oil by volume, the degradation rate in soil is fairly independent of oil concentrations. However, as oil concentration rises, the first order degradation rate decreases and the oil degradation half-life increases. Ultimately, when the oil reaches saturation conditions in the soil (i.e., 30-50% oil), biodegradation virtually ceases (Eastcott et al. 1989). This is substantiated by Borden et al. (1986) who found that biodegradation of trace quantities of hydrocarbon compounds occurred along contaminant plume edges in the presence of oxygenated formation water, but that little biodegradation occurred in the plume center where concentrations were higher. Wilson et al. (1985) also found biodegradation to take place selectively along plume margins controlled by the oxygen supply.

The point at which biodegradation starts to become adversely affected by the amount of oil present is not well established. Other inhibitory effects include the generation of toxic intermediate organic compounds. Degradation of aromatic hydrocarbons, such as toluene, can yield phenolic and benzoic acid intermediates. Various microbial populations may be inhibited by compounds such as phenol and toluene, particularly at high concentrations. Although phenol- and toluene-degrading microorganisms have been isolated in soil exposed to low concentrations of these compounds, they are biocidal at elevated concentrations (Frankenberger 1992).

The inhibitory effects of heavy metals can also influence biodegradation of organic materials. The presence of heavy metals in oil sludge, motor oil, and used crankcase oil may have deleterious effects on the hydrocarbon oxidizers in decomposing petroleum hydrocarbons (Frankenberger 1992). Jensen (1977) studied the effects of lead on biodegradation of oily waste in soil and found that the presence of lead caused certain changes in the population of soil microbiota. Reduction in the bacterial population was evident, particularly at the highest lead concentration of 5,000 ppm. Measurements of oxygen consumption revealed increased microbial activity after the addition of oil to soils, but the presence of lead markedly reduced this activity with a prolonged lag phase in the biodegradation of oil sludge. Other elements of concern include zinc, copper, chromium, nickel, and cadmium. With repeated applications of oily sludge to a landfarm operation, heavy metals may accumulate at levels in which biodegradation may be reduced.

### 5.3.3 Models

An understanding of the factors that affect the fate and transport of contaminants in the environment, and the ability to develop and apply mathematical models that incorporate these factors, are important in risk management applications. Models are used to approximate real world processes to provide environmental analyses to support management decisions. If properly used, models can assist decision makers in effectively dealing with the complex issues related to petroleum releases in the environment.

As noted earlier, petroleum products released to the environment migrate through soil by two general pathways: via bulk oil flow and as individual compounds dissolved in air or water. Although comprehensive mathematical models could be devised to treat both types of migration, the resultant framework would likely be excessively complex. Eastcott et al. (1989) suggests a two-stage modeling approach. The first stage considers transport of the bulk oil phase. After the oil is rendered immobile, a second stage is applied to assess the fate of the individual compounds that separate from the bulk phase. Models of this sort are often called solute transport models. The use of a two-stage approach is justified because when bulk oil flow does occur, it results in little or no component separation (i.e., benzene travels as fast as hexane) and the transport rate is usually fast relative to that of the dissolution rate (Eastcott et al. 1989).

Modeling the bulk oil phase is complex and includes many uncertainties; consequently, it has not been employed extensively in decision-making processes (Bonazountas 1988). One exception is the Hydrocarbon Spill Screening Model (HSSM), which simulates the flow of LNAPLs through the unsaturated zone, LNAPL spreading in the capillary fringe, and the transport of a single chemical originating from the LNAPL in the water table aquifer (Charbeneau et al. 1995). HSSM may be used to provide an estimate of dissolved concentrations of compounds originating from a petroleum release of known composition, rate of release, and volume of release. It is generally assumed that modeling interest lies in the potential for adverse impacts to water quality, and most modeling practices have concentrated on the behavior of dissolved organic compounds at the edges of bulk oil plumes or lenses. Table 5-6 lists selected soil and groundwater models that are well documented, operational, and representative of types of available models.

**Table 5-6. Selected Soil and Groundwater Models**

Model	Model category	Description
PRZM-2	Unsaturated zone/groundwater	PRZM-2 is a combination of two models developed to simulate the one-dimensional movement of pesticides. It has been used predominantly for evaluation of pesticides in the root zone.
SESOIL	Unsaturated zone	SESOIL is a one-dimensional, finite difference flow and transport model. The model estimates the rate of vertical solute transport and transformation from the land surface to the water table.
VLEACH	Unsaturated zone	VLEACH is a one-dimensional, finite difference model developed to simulate the transport of contaminants displaying linear partitioning behavior through the vadose zone to the water table by aqueous advection and diffusion.
MULTIMED	Unsaturated zone/groundwater	MULTIMED was developed as a multimedia fate and transport model to simulate contaminant migration from waste disposal units. Release to either air or soil, including the unsaturated and the saturated zones, are possible interception of the subsurface contaminant plume by a surface stream are included.
M3TD	Groundwater	MT3D is a transport model that simulates advection, dispersion, source/sink mixing, and chemical reactions of contaminants in groundwater flow systems in either two or three dimensions.
MODFLOW	Groundwater	MODFLOW is a three-dimensional finite-difference groundwater flow model. This model analyzes groundwater flow under various hydrologic conditions, including a combination of hydrogeologic layers and external stresses.
PATH3D	Groundwater	PATH3D is a general particle tracking program for calculating groundwater paths and travel times in steady-state or transient, two- or three-dimensional flow fields. This program is particularly useful for delineating contaminant capture zones or wellhead protection zones.
CHEMFLO	Unsaturated zone	CHEMFLO is a one-dimensional flow and transport model designed to simulate the movement of water and chemicals into and through soils.
MINTEQ	Geochemical	MINTEQ is a geochemical model designed to estimate equilibrium compositions of dilute aqueous solutions.
HSSM	Unsaturated zone/groundwater	HSSM simulates the flow of light nonaqueous phase liquids (LNAPLs) through the unsaturated zone, spreading in the capillary fringe, and transport of chemical constituents originating from the LNAPLs in the water table aquifer.
SCDM	Ranking	

Source: Bonazountis 1988, 1991; Charbeneau 1995; Daugherty 1991

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## 5.3.3.1 Transport Equations

Using the fraction method, hydrocarbon fractions are established on the basis of compounds having similar leaching and volatilization factors. The TPHCWG (1997b) used equations from the *Standard Guide for Risk-Based Corrective Action (RBCA) Applied to Petroleum Release Sites* (ASTM 1995) to estimate the volatilization factor and leaching factor. These equations are shown below.

$$\text{Volatilization Factor} = \frac{\left[\frac{\text{mg}}{\text{m}^3} - \text{air}\right]}{\left[\frac{\text{mg}}{\text{kg}} - \text{soil}\right]} = \frac{H\rho_s}{[\theta_{ws} + K_s\rho_s + H\theta_{as}] \left[1 + \frac{U_{\text{air}}\delta_{\text{air}}L_s}{D_{\text{eff}}W}\right]} \times 10^3 \quad [5-1]$$

$$\text{Leaching Factor} = \frac{\left(\frac{\text{mg}}{\text{L}} - \text{H}_2\text{O}\right)}{\left(\frac{\text{mg}}{\text{kg}}\right) - \text{soil}} = \frac{\rho_s}{[\theta_{ws} + K_s\rho_s + H\theta_{as}] \left[1 + \frac{U_{\text{gw}}\delta_{\text{gw}}}{IW}\right]} \times 10^0 \quad [5-2]$$

where

- $\rho_s$  = soil bulk density (g/cm<sup>3</sup>)
- $\theta_{\text{as}}$  = volumetric air content in vadose zone soils (cm<sup>3</sup>/cm<sup>3</sup>)
- $\theta_{\text{ws}}$  = volumetric water content in vadose zone soils (cm<sup>3</sup>/cm<sup>3</sup>)
- $U_{\text{air}}$  = wind speed above ground surface (c/s)
- $\delta_{\text{air}}$  = ambient air mixing zone thickness (cm)
- $L_s$  = depth to subsurface soil sources (cm)
- $W$  = width of source area parallel to groundwater flow direction (cm)
- $U_{\text{gw}}$  = groundwater Darcy velocity (cm/yr)
- $\delta_{\text{gw}}$  = groundwater mixing zone thickness (cm)
- $I$  = infiltration rate of water through soil (cm/yr)
- $K_s$  = soil-water sorption coefficient ( $f_{\text{oc}} K_{\text{oc}}$ ) (cm<sup>3</sup>/g)
- $H$  = Henry's law constant (cm<sup>3</sup>/cm<sup>3</sup>)
- $D_{\text{eff}}$  = effective diffusion coefficient through soil (cm<sup>2</sup>/s)

In accordance with the RBCA conceptual models, the leaching factor and the volatilization factor were estimated for 260 compounds present in petroleum distillates and crude oil.

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**5.3.3.2 Estimating Physical and Chemical Properties**

Solution of equations 5-1 and 5-2 requires site-specific values as well as chemical-specific values. Critical chemical-specific properties in the above equations are the Henry's law constant (H), the organic carbon/water partition coefficient ( $K_{oc}$ ), and the effective diffusion coefficient through soil ( $D_{eff}$ ). Henry's law constants are estimated using solubility and vapor pressure values obtained from data compilations. The  $K_{oc}$  is estimated from the octanol-water coefficient ( $K_{ow}$ ) and is commonly estimated from the Hansch and Leo (1979) fragment constant approach (TPHCWG 1997b):

Diffusivity in air ( $D_{air}$ ) for compounds where experimental data were unavailable can be calculated using the following equation:

$$D_{air-B} = \frac{J_B}{\nabla X_B} \quad [5-3]$$

where

$D_{air-B}$  = diffusivity of compound B in air ( $\text{cm}^2/\text{s}$ )

$J_B$  = net molal flux of B ( $\text{mol}/\text{cm}^2\text{-s}$ )

$X_B$  = concentration gradient of B ( $\text{mol}/\text{cm}^3\text{-cm}$ )

For a more detailed descriptions of  $K_{oc}$  and diffusivity refer to TPHCWG (1997b).

The TPHCWG correlated chemical-specific leaching factors and volatilization factors for hydrocarbon compounds present in gasoline and crude oil with the Carbon Number Index, which is defined as the boiling point normalized to the *n*-alkanes. The correlation to Carbon Number Index was used because it closely follows chemical behavior in the boiling point gas chromatograph column and because the literature indicates that the various properties should be well correlated to this index (Gustafson 1995).

The leaching and volatilization behavior of the hydrocarbon compounds spans many orders of magnitude. Compounds exhibiting similar leaching and volatilization factors were grouped into carbon fractions by the TPHCWG. Compounds were assigned to a given fraction within aliphatic and aromatic groupings on the basis of having leaching and volatilization factors within

approximately one order of magnitude (TPHCWG 1997b). A set of 13 fractions were selected by the TPHCWG for use in evaluating TPH environmental levels (TPHCWG 1997b).

### 5.3.3.3 Transport Models

Transport models fall into four main categories:

- unsaturated zone,
- groundwater,
- geochemical, and
- ranking

The first two categories use similar methodologies applied to different geohydrologic conditions; the third estimates chemical concentrations at equilibrium; and the fourth serves as a screening methodology to evaluate the severity of a release. As shown in Table 5-6, the majority of the models are geared toward assessing contaminant behavior in the unsaturated zone and groundwater. These types of models can appropriately be used for assessing petroleum release sites, but it is important to note that they have been developed for the broad spectrum of contaminants typically found at Superfund sites (e.g., chlorinated hydrocarbons and metals) and have not always been verified or validated for petroleum hydrocarbons in natural porous media (Daugherty 1991). For example, well known and available models such as SESOIL, which is a one-dimensional, finite difference flow and transport model developed for evaluating the migration of contaminants through the unsaturated zone, cannot simulate the transfer of hydrocarbon compounds from the bulk oil phase to the dissolved aqueous phase.

Despite their limitations, models are useful for assessing generic effects of contaminants or impacts over larger areas. For this purpose, however, simplified expressions derived from first principles appear to be as useful as more elegant computer models for the evaluation of contaminant fate and transport at small sites.

For purposes of this section, the chemical-specific parameters for the petroleum hydrocarbon fractions are based on selecting a midpoint for the fraction, based on empirical data unified by equivalent carbon number (EC). The fractions labeled as C<sub>5</sub>-C<sub>7</sub> and >C<sub>7</sub>-C<sub>8</sub> are characterized by one compound only, benzene and toluene, respectively. Remaining fractions are characterized by multiple



compounds, as described in TPHCWG (1997b). Representative physical parameters for TPH fractions are presented in Table 5-7.

ASTM's risk-based corrective action (RBCA) uses a tiered approach to data collection and analysis in supporting decisions on site assessment and response to petroleum. The RBCA procedure begins with the assessment of the site (see Figure 5-2 for RBCA process flow-chart).

As part of Tier 1, a look-up table is used to determine whether site conditions satisfy the criteria for a quick regulatory closure or warrant a more site-specific assessment. The look-up table is a tabulation for potential exposure pathways, media (i.e., soil, water, and air), a range of incremental carcinogenic risk levels and hazard quotients equal to unity, and potential exposure scenarios for each chemical of concern. In Tier 2, the non-site-specific assumptions and point(s) of exposure (point at which an individual or population may come in contact with a chemical of concern originating from a site) used in Tier 1 are replaced with site-specific data and information. In Tier 2, the user applies Tier 1 risk-based screening levels (RBSL) look-up table values for the direct exposure scenario at reasonable point(s) of exposure (as opposed to the source areas as is done in Tier 1). The additional site-specific data may support alternate fate and transport analysis. Tier 2 RBCA process also involves the development of site-specific target levels (SSTLs) based on the measured and predicted attenuation of the chemical(s) of concern away from the source using relatively simplistic mathematical models. In Tier 3 evaluation, SSTLs for the source area(s) and the point(s) of compliance are developed on the basis of more sophisticated statistical and contaminant fate and transport analysis using site-specific input parameters for both direct and indirect exposure scenarios. Tier 3 evaluation is much more complex than Tiers 1 and 2 since it may include additional site assessment, probabilistic evaluations, and sophisticated chemical fate/transport models.

#### **5.4 LEVELS IN THE ENVIRONMENT**

It is extremely difficult to make general statements about typical TPH or TPH-component levels in environmental media. Environmental fate and transport processes of TPH mixtures are complex. Interactions of the chemicals within the bulk oil typically result in different environmental fate and transport than would be predicted for the individual components. As with the discussion of basic fate and transport processes (see in Section 5.3), site-specific information is nearly always needed for

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**Table 5-7. Representative Physical Parameters for TPH Fractions, Based on Correlation to Relative Boiling Point Index**

Fraction	Solubility, mg/L	Vapor pressure, atm	Henry's law, cm <sup>3</sup> /cm <sup>3</sup>	Log K <sub>oc</sub>
<b>Aliphatics</b>				
EC <sub>5</sub> -EC <sub>6</sub>	36	0.35	47	2.9
EC <sub>&gt;6</sub> -EC <sub>8</sub>	5.4	0.063	50	3.6
EC <sub>&gt;8</sub> -EC <sub>10</sub>	0.43	0.0063	55	4.5
EC <sub>&gt;10</sub> -EC <sub>12</sub>	0.034	0.00063	60	5.4
EC <sub>&gt;12</sub> -EC <sub>16</sub>	0.00076	0.000076	69	6.7
EC <sub>&gt;16</sub> -EC <sub>35</sub>	0.0000025	0.0000011	85	8.8
<b>Aromatics</b>				
EC <sub>5</sub> -EC <sub>7</sub> <sup>a</sup>	220	0.11	1.5	3.0
EC <sub>&gt;7</sub> -EC <sub>8</sub> <sup>b</sup>	130	0.035	0.86	3.1
EC <sub>&gt;8</sub> -EC <sub>10</sub>	65	0.0063	0.39	3.2
EC <sub>&gt;10</sub> -EC <sub>12</sub>	25	0.00063	0.13	3.4
EC <sub>&gt;12</sub> -EC <sub>16</sub>	5.8	0.000048	0.028	3.7
EC <sub>&gt;16</sub> -EC <sub>21</sub>	0.65	0.0000011	0.0025	4.2
EC <sub>&gt;21</sub> -EC <sub>35</sub>	0.0066	0.00000000044	0.000017	5.1

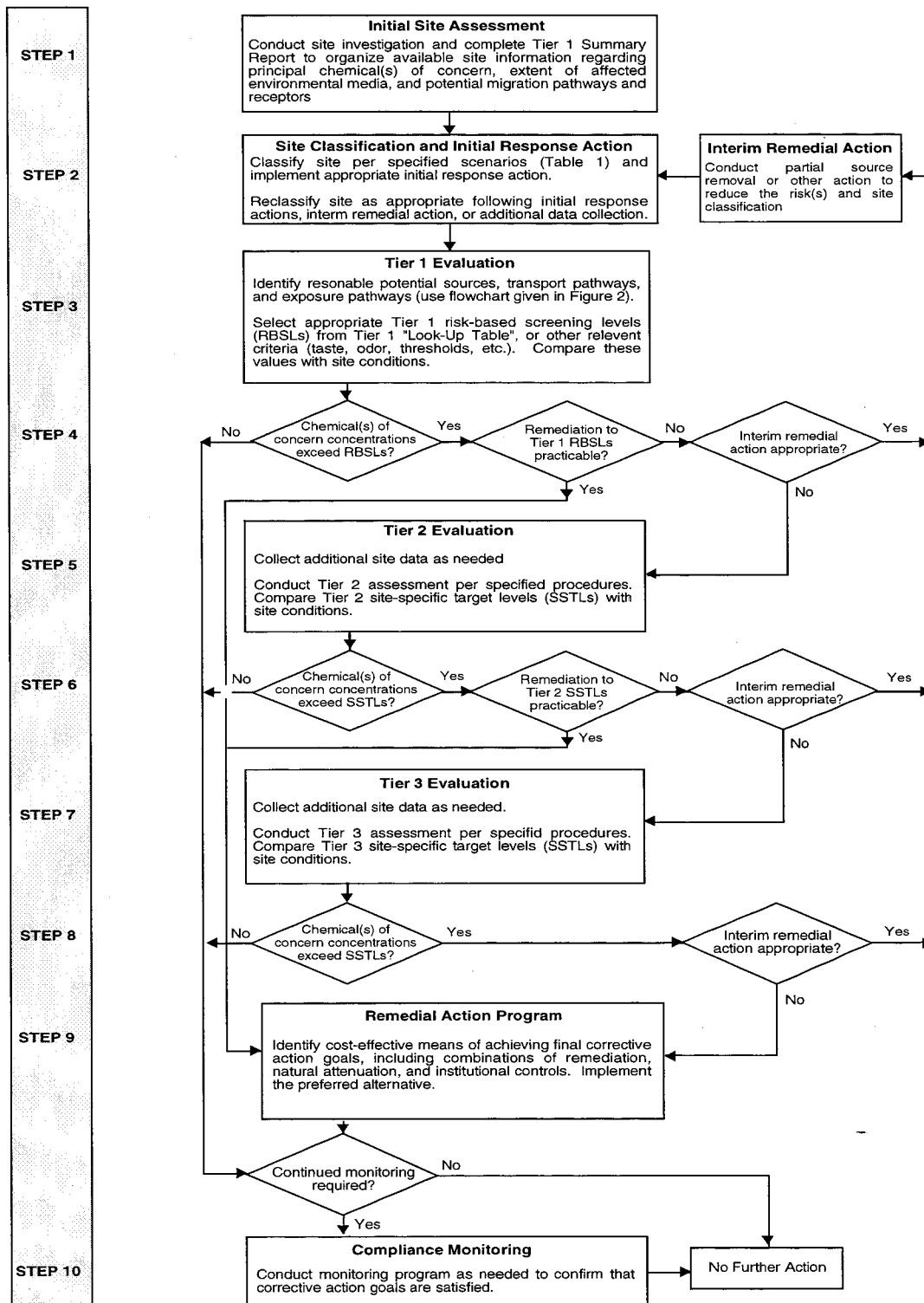
<sup>a</sup> The only compound contained in this fraction is benzene.

<sup>b</sup> The only compound contained in this fraction is toluene.

Source: TPHCWG 1997b

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Figure 5-2. Risk Based Corrective Action Process Flow Chart



Source: ASTM 1995

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correct interpretation of data for such media as surface water, soils, or groundwater. Petroleum site contaminants, especially the types of bulk fuel products and lubricants that are the focus of this profile, are usually encountered as liquids or semi-liquid sludges. The site contaminants almost always originate as mixtures of many different hydrocarbons typical of such initial products as motor gasoline, jet fuels, or fuel oils. Frequently, there are portions of a waste site where soils or sub-soil materials have accumulated large masses of petroleum contaminants that form nonaqueous liquid systems. The term nonaqueous phase liquids (NAPL) is often applied to such areas of heavy contamination. NAPLs propagate plumes moving away from the central mass. The NAPL complex, consisting of the central mass and plumes, usually reaches an equilibrium due to a combination of physical, chemical, and biochemical processes. TPH chemicals move into the actual soil or groundwater media from the edge of the NAPL plumes.

Without some knowledge of the locations of NAPL central masses or plumes at a waste site, it can be very hard to interpret analyses from soil samples or test wells. Within the NAPL zone, readings for TPH or one or more specific petrochemicals may be very high. Such high readings are indicative of a soil matrix virtually engulfed by a petroleum waste and represent the bulk oil product rather than the environmental media. Beyond the NAPL zone, the observed levels are substantially less. Media sampling values taken at random from different site-specific spatial contexts should be interpreted within the context of the sampling location relative to the NAPL central masses and plumes.

Since most TPH contamination involves a complex mixture of hydrocarbons, it is unlikely that aqueous readings beyond the NAPL zone will be near the limits of solubility (based on assumptions of a pure hydrocarbon type in equilibrium with water). If concentrations are near or above solubility limits, NAPL was probably present in the sample. TPH materials are relatively insoluble in water, with only the BTEX chemicals or some short-chain aliphatic hydrocarbons showing any appreciable potential for water solubility. When they are part of complex mixtures, the individual components never reach the concentrations predicted from their solubility constants as individual chemicals. For example, chemicals like benzene or toluene, which may constitute a small percentage within an initial bulk product like gasoline, jet fuel, or diesel fuel, have a much greater tendency to stay dissolved in the NAPL system than to become integrated into the water-based system beyond the NAPL boundary. Therefore, the effective solubility of these chemicals as part of a complex mixture is less than it would be in a release of the pure chemical.

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Some simple examples help illustrate this point. A study by Burris and MacIntyre (1984) compared the theoretical solubilities of specific chemicals in water to the solubilities of the same chemicals when they were part of such petroleum product mixtures as JP-4 jet fuel. The results are summarized in Table 5-8. Similar comparisons for all the BTEX (benzene, toluene, ethylbenzene, xylene) chemicals, based on materials presented by Potter (1993) are presented in Table 5-9.

The information presented in Tables 5-8 and 5-9 shows that for common petroleum products in water, the solubility of the component chemicals is usually less than the potential solubility of the individual chemical in water by an order of magnitude or more. Table 5-9 also shows why much attention often focuses on site contamination involving gasoline. Gasoline mixtures have much higher percentages of light fraction aromatic hydrocarbons, such as the BTEX aromatics, than other bulk fuel products. This can lead to much higher levels of contamination in ambient water or groundwater from gasoline than from petroleum mixtures with less soluble components. The increased solubilities of the BTEX chemical components from gasoline mixtures would thus be more likely to result in groundwater contamination. For other bulk fuel products, BTEX levels in the mixture are generally far lower; as a result, their water solubility and thus, their potential for groundwater contamination, would be much lower.

In light of these considerations, it becomes easier to see why it is highly desirable that available monitoring data from environmental media be combined with site-specific information. The basic needs are locational data on the spatial configuration of NAPL pockets and plumes combined with analyses of the types of TPH components found in the NAPL system and the surrounding, relatively uncontaminated media (soils, water, and groundwater). With this basic knowledge, a variety of modeling techniques can be applied to estimate effective solubilities of specific hydrocarbon compounds (Feenstra et al. 1991). Moreover, since there can be literally thousands of specific compounds in TPH site contaminants, it is improbable that a site analysis for a TPH-contaminated site would include sampling data for all TPH components. As a result, the surrogate approaches and screening modeling tools such as RBCA have been widely used to evaluate environmental data at TPH-contaminated waste sites.

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**Table 5-8. Comparison of Select Hydrocarbon Solubilities for JP-4**

Compound	Solubility of pure compound in water (mg/L)	Solubility in water when part of JP-4 (mg/L)
Toluene	576.0	28.3
Ethyl benzene	180.0	10.6
n-Octane	0.884	0.173

Source: Burris and MacIntyre 1984

**Table 5-9. Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX) Concentrations in Water Equilibrated with Various Petroleum Products**

Product	Benzene (mg/L)	Toluene (mg/L)	Ethylbenzene (mg/L)	Xylenes (mg/L)
Gasoline	29.5	42.6	2.4	14.7
Diesel fuel	0.13	0.41	0.18	0.70
#6 Fuel oil	0.01	0.03	0.007	0.05
Drinking water standard	0.005 (MCL)	2.0 (MCLG)	0.66 (MCLG)	0.44 (MCLG)
Pure chemical and water	820.0	576.0	180.0	220.0 (160–220)

MCL = maximum contaminant level; MCLG = maximum contaminant level guidelines

Source: Potter 1993

## 5.5 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 TPH 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 TPH.

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.

### 5.5.1 Identification of Data Needs

**Physical and Chemical Properties.** The physical and chemical properties of some TPH compounds and petroleum products containing TPH are well defined and can be used to estimate the fate of TPH transport fractions following release to the environment (Air Force 1989, 1991; IARC 1987, 1989a, 1989b, 1989c, 1989d). Data needs associated with specific TPH compounds that are components of petroleum products (benzene, ethylbenzene, toluene, xylenes, hexane, and PAHs) are presented in the ATSDR toxicological profiles for these chemicals (ATSDR 1994, 1995d, 1995f, 1997a, 1999a, 1999b).

**Production, Import/Export, Use, Release, and Disposal.** TPH compounds are the primary component in various petroleum products; therefore, most releases of TPH occur as a result of petroleum product spills either on land or water. More information on the production volumes for various petroleum products, environmental releases, and disposal would aid in assessing the potential for human exposure to TPH as a result of accidental or intentional release. Data needs for specific petroleum products are discussed in the ATSDR toxicological profiles for automotive gasoline (1995a), Stoddard solvent (1995b), jet fuels (1995c and 1998b), fuel oils (1995g), hydraulic fluids (1997b), and mineral-based crankcase oil (1997c).



**Environmental Fate.** The environmental fate of TPH is based on the environmental partitioning of the major hydrocarbon fractions. However, the environmental fate of chemicals in mixtures and/or bulk oil releases may be different than that observed for releases of individual TPH chemicals (see Sections 5.3.2.1 and 5.3.2.2). The more soluble and volatile fractions (i.e., the low molecular weight aliphatic and aromatic fractions) are more likely to leach to groundwater, volatilize to the air, or biodegrade than the larger TPH compounds are. These higher molecular weight compounds tend to sorb to the soil and persist at the site of release. The movement and persistence of several TPH compounds and petroleum products are well studied. Data needs for specific TPH compounds and petroleum products have been discussed in other ATSDR toxicological profiles (ATSDR 1994, 1995a, 1995b, 1995c, 1995d, 1995e, 1995f, 1995g, 1997a, 1997b, 1997c, 1998b, 1999a, 1999b).

**Bioavailability from Environmental Media.** The extent of absorption of TPH by inhalation, oral, and/or dermal routes varies because of the wide range of physical/chemical properties observed for these chemicals. The extent of absorption by the various routes depends on the volatility, solubility, lipophilicity, and other properties of the specific TPH chemical or mixture. Several of the TPH component compounds have been discussed in individual ATSDR toxicological profiles (e.g., benzene, ethylbenzene, toluene, xylenes, hexane, PAHs), which should be consulted for further information (ATSDR 1994, 1995d, 1995f, 1997a, 1999a, 1999b). More data linking exposure levels of TPH mixtures 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 TPH.

**Food Chain Bioaccumulation.** Studies of the accidental and intentional release of gasoline and fuel oils to the aquatic environment indicate that aquatic organisms are able to bioaccumulate some TPH fractions, particularly PAHs (Air Force 1989; Farrington et al. 1982); however, depuration does occur if the source of the contamination is removed (Cox et al. 1975; Williams et al. 1989). In general, the lower molecular weight aliphatics and aromatics do not bioaccumulate (Air Force 1989). Further studies are needed to determine the biomagnification potential of the TPH fractions, 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 PAHs (ATSDR 1994, 1995d, 1995f, 1997a).

## 5. POTENTIAL FOR HUMAN EXPOSURE

Research on the biomagnification of various petroleum products (e.g., gasoline, fuel oil) would not be useful because the composition of these mixtures changes rapidly in the environment. Individual chemicals present in the original mixture may bioaccumulate, but the mixture does not.

**Exposure Levels in Environmental Media.** TPH is commonly measured where hydrocarbon releases have occurred (e.g., leaking gasoline, diesel, or fuel oil tanks and petroleum product spills). In most cases, the analytical method does not provide specific information regarding the TPH fractions present (see Section 3.3). More data on levels of TPH fractions and/or their components in the air, water, and soil around facilities where petroleum products 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 petroleum products in manufacturing and those involved in their transfer may experience increased dermal and inhalation exposures to TPH. Workers in the petroleum refining industry, particularly those involved with monitoring and servicing unit equipment, are known to have increased exposure to TPH (Runion 1988). Reliable monitoring data for levels of TPH in contaminated media could be used in combination with biomarkers to identify TPH exposure and assess the potential risk of adverse health effects in populations living near contaminated areas. This information is necessary for assessing the need to conduct health studies on these populations.

**Exposure Registries.** No exposure registries for TPH or petroleum products 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. A registry does exist for benzene, a component of TPH. More information on the benzene exposure registry can be found in the ATSDR toxicological profile for benzene (ATSDR 1997a).

### 5.5.2 Ongoing Studies

No summary of ongoing studies is presented in this profile. Useful summaries are provided in toxicological profiles for the specific petroleum hydrocarbons or petroleum products, as listed in Table 3-1. As of September 1999, a 90-day toxicity study of a C<sub>9</sub> to C<sub>16</sub> aromatic fraction in rats and mice was completed by Dr. D. Mattie and colleagues at Wright Patterson toxicology laboratory (DOD), though not published. No other petroleum fraction toxicity research can be reported.