

## 5. POTENTIAL FOR HUMAN EXPOSURE

### 5.1 OVERVIEW

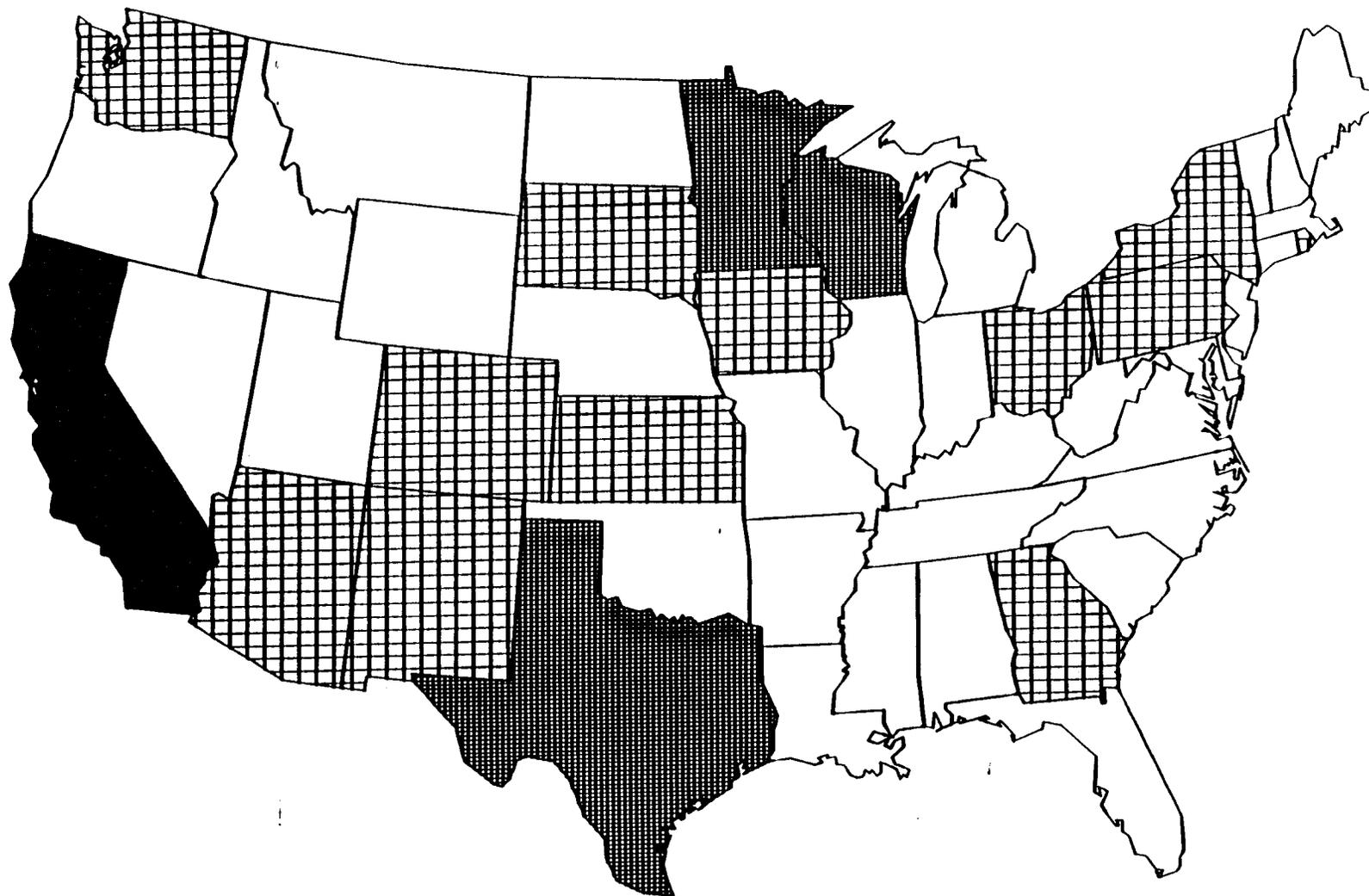
Gasoline is a mixture of relatively volatile hydrocarbons, including alkanes, cycloalkanes, alkenes, and aromatics. Individual hydrocarbon components differentially partition to environmental media on the basis of their physical/chemical properties. Gasoline is released to the atmosphere as hydrocarbon vapors from processing and use as a fuel, and to surface water, groundwater, and soil through spills and leaks in aboveground and underground storage tanks and pipelines. Gasoline has been identified in 23 of the 1,397 NPL hazardous waste sites that have been proposed for inclusion on the NPL (HAZDAT 1992). The frequency of these sites within the United States can be seen in Figure 5-1.

The volatile hydrocarbon fraction of gasoline, which consists primarily of short-chain ( $C_4$ - $C_5$ ) alkanes and alkenes and some aromatics, partitions to the atmosphere where photochemical oxidation is the main removal process. Much of what is released to surface waters and surface soils is lost by volatilization to the atmosphere. Releases to subsurface soils may leach through the unsaturated zone and contaminate groundwater. Aromatics constitute most of the water soluble fraction of gasoline. Biodegradation of gasoline hydrocarbons by a diverse group of microorganisms is an important removal process in surface waters, soil, and groundwater. Bioconcentration and sorption of gasoline hydrocarbons to soils and sediments may be important only for higher molecular weight hydrocarbons that are resistant to biodegradation.

Exposure of the general population to gasoline occurs primarily through inhalation of very small quantities of the volatile fraction of the mixture during automobile refueling. Another important source of exposure is ingestion, dermal, and inhalation exposure for certain populations through the use of gasoline-contaminated surface water or groundwater in domestic potable water applications. Inhalation also appears to be the main route of occupational exposure for individuals employed in the petroleum and automotive industries. Populations with potential exposures to gasoline hydrocarbons

FIGURE 5-1. FREQUENCY OF NPL SITES WITH GASOLINE CONTAMINATION \*

GASOLINE



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FREQUENCY



1 SITE  
5 SITES



2 SITES

\*Derived from HazDat 1994

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include individuals living in the vicinity of gasoline service stations or tank farms or near leaking underground storage tanks.

### 5.2 RELEASES TO THE ENVIRONMENT

#### 5.2.1 Air

Gasoline vapors are released to the air during refueling of gasoline-powered vehicles (Kearney and Dunham 1986; McDermott and Vos 1979; Shiller 1987), bulk transfer of gasoline at distribution terminals (Irving and Grumbles 1979; Kawai et al. 1991; Phillips and Jones 1978), leaks from storage containers and loading equipment (Dell'Acqua et al. 1976; Phillips and Jones 1978), and during removal and maintenance of underground storage tanks (Kramer 1989; Shamsky and Samimi 1987). Volatile hydrocarbons in gasoline spilled on soil or surface water will rapidly evaporate, contributing to air contamination (Kramer 1989; Phillips and Jones 1978; Van Gelder-Ottway 1976).

Releases of small amounts of gasoline vapors have been shown to occur at service stations during refueling of vehicles. Most of the release comes from displacement of hydrocarbon vapors during filling of the vehicle or the underground storage tank. Some release will also occur from spills and line leaks. Gasoline vapor levels measured in the air (personal air samples) at a high-volume service station in Pennsylvania during 1 week in May ranged from 0.9 to 116.3 mg/m<sup>3</sup>. The highest levels generally were found within the immediate vicinity of the fuel nozzle during refueling operations and levels decreased with distance from the pump, indicating that considerable release occurs during vehicle refueling (Keamey and Dunham 1986).

Releases of gasoline vapors during bulk transfer operations occur primarily via displacement of hydrocarbon vapors from the tanker by the liquid gasoline (Irving and Grumbles 1979; Phillips and Jones 1978). Other sources of release include leaks in fill lines and spills. The amount released during transfer operations will vary with the method used. Loading operations employing vapor recovery systems do not release as much vapor as those not utilizing them. Measurements taken at five plants located in the south, southwest, midwest, and west coast area during May and June showed lowest releases in top or bottom loading operations with vapor recovery systems (Phillips and Jones

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1978). Samples taken during top-loading had levels of 25 ppm or less in 98% of the samples while levels of 110 ppm or less were found in 90% of the samples taken during bottom-loading. In contrast, loadings without vapor recovery systems were considerably higher. Ninety percent of the samples from both the top- and bottom-loaded samples with no vapor recovery had levels of 225 ppm or less. Measurements of benzene (used as an indicator of gasoline vapor release) taken at plants in the east, southeastern, and southwestern United States confirm that releases occur during bulk transfers (Irving and Grumbles 1979). Ninety-five percent of samples from top-loading facilities without vapor recovery systems had benzene levels below 8.5 ppm. At bottom-loading facilities without vapor recovery, 95% of the samples were below 3.5 ppm. At bottom-loading facilities with vapor recovery, 95% were below 1.8 ppm. Release from underground storage tanks during removal and maintenance procedures has been documented by personal monitoring and area sampling (Kramer 1989; Shamsky and Samimi 1987). Measurements of total hydrocarbons in the vicinity of tank excavation and maintenance operations have ranged from 0.64 ppm upwind from the removal site to 860 ppm during inerting (addition of dry ice to the tank to remove hydrocarbon vapors and lower the oxygen content) (Shamsky and Samimi 1987). An area sample taken during transfer of gasoline from the storage tank to a tank truck contained 11 ppm of total hydrocarbons (Kramer 1989). Release of vapors occurs during all phases of the operation including transfer of gasoline from the storage tank, washing of the interior and removal of vapors, excavation, and examination and maintenance (Kramer 1989; Shamsky and Samimi 1987). Gasoline vapors will also be released from soil at the site contaminated by spillage of gasoline (Kramer 1989). Gasoline is not listed on the Toxics Release Inventory; however, several of the component hydrocarbons are listed. Refer to the ATSDR toxicological profiles for benzene, toluene, xylene, and ethylbenzene (ATSDR 1989, 1990, 1991) for information on these individual hydrocarbon components of gasoline.

### 5.2.2 Water

Gasoline can migrate to groundwater from the soil surrounding leaking underground storage tanks and pipelines. By one estimate, as many as 75,000-100,000 tanks leak millions of gallons of gasoline to groundwater each year (Feliciano 1984; Tanglely 1984). This estimate does not include leakage from abandoned tanks. One leak reported in a Michigan 1997-1979 survey resulted in the release of over 60,000 gallons of gasoline to groundwater (Feliciano 1984). The state of Maine estimates that leaking

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underground storage tanks are responsible for the release to groundwater of about 11 million gallons of gasoline yearly (Feliciano 1984). Gasoline in underground drainage water and sump water from a basement have been traced to leaking underground storage tanks at service stations (Dell'Acqua et al. 1976). Gasoline from an unidentified source was found floating on the water table in Hampden Township, Pennsylvania (McKee et al. 1972). A leak from a pipeline or underground storage tank contaminated groundwater in the north Los Angeles area of California with an estimated 100,000-250,000 gallons of gasoline (McKee et al. 1972). Although the total amount of gasoline released by leaking underground tanks throughout California is unknown, it has been estimated that the majority of reported leaky tanks (11,000) contained gasoline (Hadley and Armstrong 1991).

Release of gasoline to seawater may occur when barges or tankers carrying the chemical ground on reefs. Grounding of a barge in Block Island Sound, Rhode Island, resulted in release of 1,900 metric tons of gasoline into the water (Dimock et al. 1980). Based on the U.S. Coast Guard National Response Center database, an estimated 48,816 gallons of gasoline were accidentally discharged to New Jersey's Newark Bay and associated major tributaries from 1982 to 1991 (Gunster et al. 1993). Gasoline is not listed in the Contract Laboratory Program Statistical Database (CLPSD) of chemicals found in groundwater or surface water at hazardous waste sites.

### 5.2.3 Soil

Release of gasoline to soil from leaking underground storage tanks and pipelines has been reported (Tangley 1984). Most releases from storage tanks and pipelines are reported as releases to groundwater because this is where evidence of a leak first appears. However, the release is actually to surrounding soil with a migration to groundwater due to gravity and water wash down. Most estimates of the amounts of the releases are based on levels found in groundwater and have been reported in Section 5.2.2. An estimated 75,000-100,000 leaking tanks release millions of gallons of gasoline per year to the surrounding soil (Feliciano 1984; Tangley 1984). This estimate does not include abandoned tanks that may be leaking. Excavation around a tank suspected of leaking showed that gasoline was seeping into the soil from the tank (Dell'Acqua et al. 1976). Gasoline is also spilled on soil during the removal and maintenance of underground storage tanks (Kramer 1989). Soil in the business section of Rockaway Beach in Queens County, Long Island, was contaminated with gasoline

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from an identified source (McKee et al. 1972). Gasoline leaking into a department store basement in Harlan, Kentucky, was traced to the city-owned service station (McKee et al. 1972).

### 5.3 ENVIRONMENTAL FATE

#### 5.3.1 Transport and Partitioning

Gasoline is a mixture of relatively volatile hydrocarbons, including normal and branched chain alkanes, cycloalkanes, alkenes, and aromatics, that vary widely in their physical and chemical properties. Liquid gasoline generally contains alkanes, aromatics, and alkenes (IARC 1989). Gasoline is formulated to meet certain product performance specifications. Each batch of gasoline is likely to have a unique chemical composition as a result of the variable composition of the petroleum starting materials and the specific types of processing methods used in the formulation of different seasonal and performance grades of the product (Cline et al. 1991; CRCS 1985; Ghassemi et al. 1984). Upon release to the environment, gasoline is not transported as a mixture; rather, the various components of the mixture selectively partition to the atmosphere, soil, or water according to their individual physical/chemical properties. Therefore, gasoline itself is unlikely to be found in different environmental media.

The volatile fractions of gasoline are released to the atmosphere during every phase of the product formulation, handling, and marketing chain, including purchase by the consumer during refueling of gasoline-powered vehicles. These fractions generally consist of short-chain aliphatic hydrocarbons, alkenes, and aromatics (Air Force 1989; CRCS 1985; NESCAUM 1989). For example, more than 75% of airborne gasoline vapors have been reported to consist of C<sub>1</sub>-C<sub>10</sub> and lighter hydrocarbons (McDermott and Killiany 1978). In the atmosphere, the components are subject to transport, dilution, dispersion, and photochemical reaction (see Section 5.3.2.1). The more water soluble of these fractions (e.g., aromatics) may also be washed out of the atmosphere in precipitation and reenter surface waters and soils. This partitioning is particularly likely for the breakdown products of atmospheric oxidation, which are more water soluble than the parent hydrocarbons (Air Force 1981; FAO 1977; Svoma and Hauzim 1984).

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Gasoline released to surface soils will differentially partition by volatilization, dissolution, or adsorption of individual constituents according to their physical/chemical properties. Gasoline exists in soil in four states: (1) as a free-moving liquid; (2) adsorbed to soil particulates; (3) dissolved in groundwater; and (4) as a vapor (NESCAUM 1989; Svoma and Hauzim 1984). Short-chain ( $C_4$ - $C_8$ ) alkanes and alkenes with high vapor pressures and low water solubilities will volatilize to the atmosphere. Results of field experiments indicate that the volatility of gasoline from contaminated soils can be enhanced by the addition of water to the soil (Donaldson et al. 1992). Evaporation may be limited by infiltration and vertical movement of the liquid product into the soil, the extent of which depends on soil porosity (Bossert and Bartha 1984). Releases of liquid gasoline to subsurface soils will also limit volatilization losses of the lower molecular weight alkanes, which may be transported to groundwater (Air Force 1989). Higher molecular weight alkanes, alkenes, cycloalkanes, and aromatics may sorb to some extent to soil particulates (Air Force 1981, 1989). Potential sorption is greatest for alkenes, followed by aromatics, cycloalkanes, and least for alkanes (Hathaway and Andrews 1990).

Components of gasoline that are not volatilized or sorbed to soil particulates will migrate downward through the unsaturated zone by gravity or leaching to the water table (DOI 1984; Yaniga 1984). Liquid gasoline, as a result of its lower kinematic viscosity, is expected to move through the unsaturated zone of the soil at a velocity 2-3 times that of water (Bouchard et al. 1990). The amount of liquid product that reaches the water table is dependent upon the amount of product released and site-specific soil and hydrogeological conditions (Yaniga 1984). For example, if the amount of gasoline hydrocarbons is small relative to the distance to the groundwater through the unsaturated zone, the hydrocarbons will probably be retained in the soil pore spaces. However, if the amount released is large relative to the distance to the groundwater, soil pore space capacity may be exceeded and bulk fluid transport to the groundwater may occur (Bouchard et al. 1990). Hydrocarbons immobilized in the unsaturated zone may be solubilized by downward moving soil water or fluctuating elevations of groundwater, and this residual material may serve as a source of contamination through leaching of solubilized components for long periods of time (DOI 1984). Water-soluble components, which consist predominantly (87-95%) of aromatics (Coleman et al. 1984), will dissolve in groundwater, whereas insoluble components will float as a separate phase on top of the water table. Water-soluble compounds, such as benzene, toluene, and xylene, show a greater potential for transport in groundwater aquifer than insoluble forms (Uchirin and Katz 1991). Gasoline-contaminated

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groundwater may serve as a source of surface water contamination in areas where groundwater discharges to surface waters (Air Force 1989).

Liquid gasoline released to surface water spreads horizontally over the surface, presenting a large surface area from which the volatile components will rapidly partition to the atmosphere (Bossert and Bartha 1984; CRCS 1985). For example, following oil spills in marine environments, hydrocarbons of carbon chain lengths up to C<sub>13</sub> have been found to be lost by volatilization within the first few days after the spill. Hydrocarbons of up to C<sub>20</sub> volatilize after a few weeks (FAO 1977). Lateral spreading also increases dissolution of the water soluble components. Spills of gasoline in high winds and heavy seas may produce emulsions which limit evaporative losses (CRCS 1985). Components not lost to the atmosphere by evaporation probably remain near the surface where they may be degraded (see Section 5.3.2.2). Higher molecular weight components (e.g., naphthalene and substituted naphthalenes) may partition to sediments (Air Force 1981).

The bioaccumulation potentials of the major components of gasoline range from low to high. Some higher molecular weight components (e.g., naphthalene and substituted naphthalenes) may be taken up by fish and domestic animals and bioconcentrated if they persist in environmental media (Air Force 1989). Alkenes have low log octanol/water partition coefficients ( $K_{ow}$ ) of about 1 and estimated bioconcentration factors (BCF) of about 10; aromatics have intermediate values (log  $K_{ow}$  values of 2-3 and BCF values of 20-200), while C<sub>5</sub> and greater alkanes have fairly high values (log  $K_{ow}$  values of about 3-4.5 and BCF values of 100-1,500) (NESCAUM 1989).

### 5.3.2 Transformation and Degradation

#### 5.3.2.1 Air

Gasoline hydrocarbons volatilized to the atmosphere quickly undergo photochemical oxidation. The hydrocarbons are oxidized by reaction with molecular oxygen (which attacks the ring structure of aromatics), ozone (which reacts rapidly with alkenes but slowly with aromatics), and hydroxyl and nitrate radicals (which initiate side-chain oxidation reactions) (Stephens 1973). Alkanes, isoalkanes, and cycloalkanes have half-lives on the order of 1-10 days, whereas alkenes, cycloalkenes, and

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substituted benzenes have half-lives of less than 1 day (EPA 1979a). Photochemical oxidation products include aldehydes, hydroxy compounds, nitro compounds, and peroxyacyl nitrates (Cupitt 1980; EPA 1979a; Stephens 1973).

### 5.3.2.2 Water

Of the hydrocarbon components of gasoline, only xylenes, trisubstituted benzenes, and naphthalenes have been reported to undergo photolysis and photooxidation in aqueous solution. Alkanes, benzenes, and monosubstituted benzenes have been found to be resistant to photolytic breakdown in aqueous systems. The rate of reaction of trisubstituted benzenes and naphthalenes is competitive with that of volatilization from surface waters (Air Force 1981).

Many of the hydrocarbon components of gasoline have been found to undergo biodegradation in surface waters and sediment (Atlas 1981; Walker et al. 1975b). Microorganisms in marine and estuarine environments, including bacteria, yeasts, and filamentous fungi, are capable of degrading petroleum and petroleum products, including gasoline. Microbial activity becomes important about 1 week after the spill or release, after initial hydrocarbon losses have occurred through volatilization and photooxidation. Alkanes are attacked more rapidly and by a greater number of species than aromatics or naphthenics, with removal in the time frame of days-to-weeks; *n*-alkanes are more easily degraded than branched chain alkanes (FAO 1977). Degradation of gasoline hydrocarbons in surface waters is expected to be rapid under conditions favorable to microbial activity; however, it may be slow or limited under unfavorable conditions, such as low pH, low temperature, low oxygen levels, or high salinity, or where populations of degrading microbes are low (Air Force 1989).

Organic pollutants have also been found to undergo biodegradation by microorganisms isolated from groundwater (Wilson and McNabb 1983). For example, a mixed population of 32 cultures of microbes isolated from groundwater contaminated with gasoline were able to degrade gasoline hydrocarbons. *Nocardia* cultures were found to metabolize most of the alkanes, whereas *Pseudomonas* cultures were responsible for degradation of most of the aromatics (Jamison et al. 1976).

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Biodegradation of gasoline in groundwater can occur under denitrifying conditions (Carroquine et al. 1992).

### 5.3.2.3 Soil

After volatilization, biodegradation and photooxidation are the most important removal mechanisms for gasoline hydrocarbons released to surface soils (Air Force 1989). Photooxidation in surface soils is less important than in surface water environments since infiltration of the liquid product into the soil will limit exposure to solar radiation (Bossert and Bartha 1984).

Biodegradation of gasoline hydrocarbons in soil by a diverse group of microorganisms has been reported by numerous investigators (Atlas 1981; Bossert and Bartha 1984; Haines and Alexander 1974; Mann and Gresham 1990; Thomas et al. 1990). Bacteria and fungi appear to be the most important hydrocarbon-utilizing microbes in soils (Atlas 1981). n-Alkanes, n-alkylaromatics, and aromatics of carbon chain length C<sub>10</sub>-C<sub>22</sub> are the most readily degradable hydrocarbons. n-Alkanes, alkylaromatics, and aromatics above C<sub>22</sub> are generally not available for metabolism by soil microbes because of their limited water solubility and solid physical state. Higher molecular weight hydrocarbons sorbed to soil particulates are also generally unavailable for metabolism by microorganisms. Hydrocarbons in the C<sub>5</sub>-C<sub>9</sub> range are biodegradable only at low concentrations since at higher concentrations they exhibit membrane-solvent toxicity to soil microbes and are generally removed by volatilization. Hydrocarbons with condensed ring structures, such as polycyclic aromatic hydrocarbons (PAHs), and cycloalkanes are relatively resistant to biodegradation (Atlas 1981; Bossert and Bartha 1984). Isoalkanes and 1,3,5-trimethylbenzene have also been reported to be resistant to biodegradation (Mann and Gresham 1990). Some of the intermediate products of metabolism (e.g., alcohols, aldehydes, and monocarboxylic acids) are more water soluble or strongly sorbed than the parent hydrocarbons (Atlas 1981; Bossert and Bartha 1984; Carlson 1981). The rate of biodegradation is highly dependent upon the amount of the hydrocarbon substrate and a number of site-specific environmental factors, including temperature, oxygen content, moisture content, nutrient content, salinity, and pH (Atlas 1981; Bossert and Bartha 1984). Degradation of hydrocarbons by soil microbes appears to be almost exclusively an aerobic

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process. The initial steps in microbial metabolism require oxygen; reference to biodegradation under anaerobic conditions is limited (Atlas 1981; Bossert and Bartha 1984; Corapcioglu and Hossain 1990).

### 5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

#### 5.4.1 Air

Several variables can influence the measured concentrations of gasoline vapor and component hydrocarbons in air. Among these are wind direction and velocity, distance from the source of the vapors, ambient temperature, duration of sampling time, the presence of vapor recovery equipment, and composition of the gasoline (McDermott and Vos 1979; Shiller 1987).

Levels of gasoline vapor have been measured in air at service stations in several areas of the country. Area air samples taken in the vicinity of a high-volume service station in Pennsylvania during 1 week in May showed concentrations of gasoline vapor ranging from not detected (detection limit of  $0.4 \text{ mg/m}^3$ , assuming a desorption volume of 1 mL solvent) to  $28 \text{ mg/m}^3$  (Keamey and Dunham 1986). Air levels of gasoline vapor measured at seven different service stations in the United States (Houston, Texas; Manhattan Beach, California; New Britain, Connecticut; New Orleans, Louisiana; Plantation, Florida; Stickney, Illinois; and Walnut Creek, California) from March to June ranged from 1.81 to 99.2 ppm (McDermott and Vos 1979). Corresponding concentrations of benzene ranged from  $<0.01$  to 1.21 ppm.

Monitoring of the storage tank removal and maintenance operation indicated relatively high levels of gasoline vapor can be found near the site of the activities (Kramer 1989; Shamsky and Samimi 1987). Area sampling at the bottom of the excavation, directly above the excavation at ground level, upwind and downwind of the site, and at the site location during inerting (i.e., flushing with carbon dioxide) indicated the highest concentrations are found in the location of the site during the inerting process when no controlled venting of the vapors is performed. The total hydrocarbon level (a measure of gasoline vapor) at the site when no vents were used was 860 ppm. With the use of vents the total hydrocarbons measured 21.8 ppm. Total hydrocarbons were also high at the bottom of the excavation site, measuring 395 ppm compared to 16.7 ppm just above the site at ground level. As expected,

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mean upwind concentrations were lower than downwind concentrations (0.64 and 3.86 ppm total hydrocarbons, respectively) and were considerably lower than concentrations at the excavation site. Levels of 0.08 ppm benzene and 4 ppm total hydrocarbons were measured in air during on-site monitoring of an underground storage tank excavation (Kramer 1989). Levels of 1.0 ppm benzene and 11 ppm total hydrocarbons were measured during the transfer of gasoline from a tank excavated for cleaning to a tanker truck (Kramer 1989). During purging of the tank, the average atmospheric concentration of benzene near the tank was 6.7 ppm (Kramer 1989). Although venting was not used in this excavation procedure, the measured levels were considerably below previous measurements (Shamsky and Samimi 1987). The reason for the discrepancy in results could not be determined. Gasoline is not listed in the CLPSD of chemicals found in soil at NPL sites only (CLPSD 1989).

### 5.4.2 Water

One day following the accidental release of 1,900 metric tons of gasoline into the water at Block Island Sound, Rhode Island, total levels of C<sub>8</sub>-C<sub>12</sub> hydrocarbons at three sites close to the spill ranged from 5 to 20 µg/L at a depth of 3.5 meters in the water column (Dimock et al. 1980). These concentrations exceeded the background levels found at sites distant from the spill. Although gasoline is known to migrate to groundwater following its release from leaking underground storage tanks and pipelines (see Section 5.2.2), no information on levels in groundwater was located.

### 5.4.3 Soil

Although methods for the detection of gasoline hydrocarbons in soil exist (see Chapter 6), no specific data on levels in soil were located. Gasoline is known to be present in soil in areas where it has been spilled and in soil surrounding leaking underground storage tanks or pipelines (Dell'Acqua et al. 1976; Kramer 1989; McKee et al. 1972). Discriminant analysis, a multivariate statistical technique, has been applied to differentiate between gasoline contaminated soils resulting from leaking underground storage tanks and those of background origin (Saentz and Pingitore 1991).

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### 5.4.4 Other Environmental Media

Data on the concentration of hydrocarbons from gasoline contamination in media other than air, water, and soil are very limited. This is due, at least in part, to the difficulty in tracing the source of hydrocarbon contamination in other environmental media such as food, fish and shellfish, and terrestrial plants and animals. Samples of bivalve mollusks collected 2 days following an accidental spill of gasoline into Block Island Sound, Rhode Island, contained low levels of gasoline compounds (Dimock et al. 1980). However, there were no adequate control samples by which to confirm background levels of these compounds in the shellfish, so it is not certain that the contamination resulted from the spill.

### 5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

The general population may be exposed to gasoline or gasoline vapors during automobile refueling procedures, refueling of gasoline-powered equipment (e.g., lawn mowers), and through the use of gasoline-contaminated surface water or groundwater. However, no specific data on exposure of the general population were located.

Possible occupational exposure to gasoline and gasoline vapors exists for workers all along the chain of gasoline production to consumer use. Workers involved in onloading and offloading gasoline at docks and bulk storage terminals; loading, driving, and delivering fuel to storage terminals and gas stations; and refueling and automotive repair operations at service stations have a large potential for exposure (Runion 1988). Workers involved in the cleanup and maintenance of underground storage tanks and service station pump equipment are also exposed to higher-than-background levels of gasoline and gasoline vapor (Runion 1988).

Several monitoring surveys of service station employees have been conducted. Personal air sample measurements of employees at a high-volume service station in Pennsylvania for 1 week in May showed geometric mean total gasoline vapor time-weighted average (TWA) exposures of employees ranged from 2.9 to 5.2 mg/m<sup>3</sup> (Keamey and Dunham 1986). Geometric mean personal short-term exposures to gasoline vapor ranged from 12.7 to 24.7 mg/m<sup>3</sup>. Actual exposure concentrations during

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refueling ranged from not detected (detection limit of 10 mg/L extraction solvent) to 116.3 mg/m<sup>3</sup>. Component analysis of personal long-term samples showed that 2-methyl butane and pentane were the most prevalent hydrocarbons and were detected in all 18 samples at concentrations ranging from 0.1 to 1.7 ppm. Another survey of service station employees conducted from March to June at seven service stations located throughout the United States (Houston, Texas, Manhattan Beach, California, New Britain, Connecticut, New Orleans, Louisiana, Plantation, Florida, Stickney, Illinois, and Walnut Creek, California) showed that mean TWA attendant exposures ranged from 3.63 to 22.3 ppm for gasoline vapor and 0.02-0.24 ppm for benzene (McDermott and Vos 1979). The high values were found at the New Britain, Connecticut service station and appeared to be due to hydrocarbon exposure from a source other than gasoline in one sample. Excluding the Connecticut results, the range of 3.63-9.26 ppm gasoline vapor was a more representative estimate of service station employee exposure. Monitoring of service station personnel responsible for refueling operations at two service stations located near a major expressway, revealed a geometric mean 8-hour TWA of 4.0 mg/m<sup>3</sup> (range of 1.1-130.3 mg/m<sup>3</sup>) (Halder et al. 1986a). Closer monitoring of these workers showed no detectable hydrocarbon exposure levels for refueling operations totaling 22 minutes or less (limit of detection = 30 µg/sample). However, for total refueling times of 27 and 354 minutes, TWA 8-hour total hydrocarbon levels ranged from 0.7 to 1.4 and from 2.1 to 4.8 mg/m<sup>3</sup>, respectively. Most of these were lighter weight (5 or less carbon atoms) hydrocarbons.

Analysis of air samples for benzene at a service station and alveolar air levels of benzene in the attendants showed that benzene levels in the breath samples taken during refueling operations were considerably higher than during times when refueling was not occurring (Brugnone et al. 1986). Alveolar concentrations ranged from 210 to 458 ng/L during refueling and from 52 to 191 ng/L when refueling was not being done. Corresponding air levels taken in the breathing zone ranged from 63 to 611 ng/L and from 20 to 77 ng/L during periods of refueling and no refueling, respectively. The higher concentrations of benzene in alveolar air in most samples may indicate that the eliminated benzene was previously absorbed and stored.

Biological monitoring of service station workers in India revealed substantially higher levels of urinary phenol when these workers were compared to persons with no known exposure to either gasoline or benzene (Pandya et al. 1975; Rao et al. 1977). Excretion of phenol in the urine can be evidence of

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benzene exposure. Since benzene is a component of gasoline and gasoline vapor, presence of excess phenol in the urine of these workers may be associated with their exposure to gasoline vapor. Of the 51 service station workers monitored, 88% had urinary phenol levels of >20 mg/L and 47% had levels >40 mg/L. Average urinary phenol excretion in unexposed subjects was reported to be 8.6 mg/L (range of 3.3-15 mg/L). Since no measurements of gasoline or benzene in the breathing zones of these subjects were taken, the excess phenol cannot be unequivocally attributed to gasoline exposure.

Monitoring surveys of workers occupationally exposed to gasoline indicate that exposure results in higher blood and urinary concentrations of lead in these workers. A group of 26 workmen employed in a petrol company in Poland were assessed for blood and urinary levels of lead associated with their exposure to gasoline (Turlakiewicz and Chmielnicka 1985). The mean blood lead levels of these workers was 25.6 µg/dL and the mean urinary lead concentration was 7.4 µg/dL. Corresponding levels in the control group were 10.6 and 2.5 µg /dL for blood and urinary levels, respectively. Mean 8-hour TWA concentrations of lead in the workplace air ranged from 0.015 to 0.205 mg/m<sup>3</sup> depending on the specific job. A similar survey of 47 service station workers in Tasmania also indicated that blood lead levels were higher in subjects occupationally exposed to gasoline (Moore et al. 1976). The mean blood lead level of the service station workers was 32.9 µg/dL compared to a mean level of 14.3 µg/dL in the control population.

A survey of workers employed at five bulk-transfer facilities, two marine loading facilities, and two service stations located near a major expressway was conducted (Halder et al. 1986a). Personal monitoring of breathing zone levels of hydrocarbons with 6 or more carbon atoms showed 8-hour TWA geometric mean exposure concentrations of 5.7 mg/m<sup>3</sup> (range of 0.8-120.8 mg/m<sup>3</sup>) for terminal workers and 4.0 mg/m<sup>3</sup> (range of 1.1-130.3 mg/m<sup>3</sup>) for service station workers. Geometric mean 8-hour TWA exposures to hydrocarbons with four carbons or more were 31.2 mg/m<sup>3</sup> (range of 1.3-237.6 mg/m<sup>3</sup>) and 89.4 mg/m<sup>3</sup> (range of 9.1-1,580.4 mg/m<sup>3</sup>) for terminal workers and marine loading facility workers, respectively. The bulk of the hydrocarbon exposure at bulk terminals and marine loading facilities (61.3-67.4%) was to lighter hydrocarbons containing four or five carbon atoms, and of these, n-butane, isobutane, n-pentane, and isopentane were responsible for most of the

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exposure. Measured geometric mean TWA levels of benzene ranged from 0.5-0.8 mg/m<sup>3</sup> for the three worker categories.

Workers involved in the removal and maintenance of underground storage tanks are exposed to both gasoline and gasoline vapor. Monitoring of workers involved in these operations showed that exposure occurred during tank draining, tank removal, cutting and cleaning, and tank testing (Kramer 1989; Shamsky and Samimi 1987). Levels of exposure during these operations were measured for personnel involved in the procedures. Highest exposure occurred during tank removal, cutting and cleaning, with levels of total hydrocarbons in the breathing zone ranging from 9 ppm over a 6-hour exposure period for an observer to 459 ppm for a 30 minute exposure period for a laborer (Kramer 1989). Levels of benzene ranging from 0.19 ppm over 5.5 hours for an observer to 4.57 ppm over 30 minutes for a laborer were also observed. Exposures to gasoline vapors were lower for workers involved in gasoline transfer and tank-testing operations. Levels in these workers ranged from 4 to 5 ppm total hydrocarbons in the breathing zone (for exposure periods of 30 minutes to 6 hours in personnel involved in gasoline transfer) to 7-12 ppm (for periods of 3.25 to 4.75 hours in the breathing zone of workers involved in tank testing). For all procedures, laborers generally had the highest exposure to gasoline vapor and observers were exposed to the lowest amounts. Exposure to gasoline was not quantified, but dermal exposure was stated to be common during the maintenance operations. Results from a similar study of tank maintenance personnel found mean breathing zone levels of total hydrocarbons of 2.3 ppm for 18-35 minutes exposure of observers and 106 ppm for 15-110 minutes exposure of laborers. Mean benzene exposure levels were 0.1 and 6.8 ppm for observers and laborers, respectively. Potential exposures for personnel upwind and downwind of the excavation site, at the bottom of the site, directly above the site at ground level, and at the site during inerting with and without vents were also determined. Highest levels were measured during inerting without vents (mean total hydrocarbons = 860 ppm) and at the bottom of the excavation (mean total hydrocarbons = 395 ppm). Data on specific hydrocarbons in the gasoline vapor suggested that exposures exceeding the TLVs could occur for pentane, n-hexane, benzene, toluene, xylene, and total hydrocarbons if workers were exposed for 8-hour periods to concentrations found at the bottom of the excavation and during inerting of tanks without vents. However, these workers would not normally encounter 8-hour continuous exposure work days.

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Breathing zone samples collected at bulk loading terminals where driver/salesmen load their own trucks showed that highest exposure occurred during loading of tanker trucks when no vapor recovery system was used (Phillips and Jones 1978). Approximately 90% of the samples had levels of hydrocarbons of 225 ppm or less. Exposure was substantially reduced when a vapor recovery system was used, with 90% of the samples having levels of 110 ppm or less during a bottom-loading operation and 98% of samples having levels of 25 ppm or less during a top-loading operation. During unloading at service stations, 98% of the samples had levels hydrocarbons of 50 ppm or less. Results from another survey where benzene was used to monitor workers at a bulk transfer facility for exposure to gasoline vapor support the reduced exposure associated with vapor recovery systems (Irving and Grumbles 1979). Ninety-five percent of samples from top-loading facilities without vapor recovery systems had benzene levels below 8.5 ppm. At bottom-loading facilities without vapor recovery, 95% of the samples were below 3.5 ppm and at bottom-loading facilities with vapor recovery, 95% were below 1.8 ppm. These data also suggest reduced exposure levels are associated with bottom-loading of tankers.

According to the National Occupational Exposure Survey conducted from 1981 to 1983 by NIOSH, 70 employees (including 7 females) in seven plants producing petroleum and coal products were potentially exposed to natural gasoline or products containing natural gasoline (NOES 1991). Most of these (63 workers) were categorized as miscellaneous machine operators and the remainder were operators of separating, filtering, and clarifying machinery. These data are based only on actual observations of the use of gasoline or of products containing gasoline in 4,490 business establishments in the United States. In view of the information on exposure presented above, these data are believed to substantially underestimate the potential occupational exposure to gasoline.

### 5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Results from surveys of service station personnel strongly indicate that general population exposure to gasoline vapor can be expected at service stations. People who refuel their own vehicles are at risk of higher exposure than those who let attendants service their vehicles. These people are also at greater risk of contacting gasoline released from leaking pump lines and overfilled tanks. Populations living in the vicinity of a service station or bulk loading terminal are expected to have higher exposure to

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volatile gasoline-related hydrocarbons than those far removed from these businesses. Higher exposure to both gasoline and its vapor is also expected during filling of tanks on machines that operate on gasoline such as gasoline-powered lawn mowers.

Populations located near underground storage tanks or pipelines are at risk of exposure to high levels of gasoline-associated hydrocarbons through ingestion of contaminated drinking water. Additional inhalation and dermal exposure would come from other water uses such as washing dishes and showering. These populations may also be exposed to higher than background levels of gasoline vapor that may seep into basements.

Workers employed in occupations in which gasoline is transferred between various storage containers, such as those employed at bulk transfer facilities or marine loading facilities, tanker truck drivers, and service station employees, are exposed daily to higher levels of gasoline and gasoline vapor. Workers employed in occupations responsible for location of leaks, remediation of spills and leaks, and removal and maintenance of underground storage tanks are also potentially exposed to high levels of gasoline and gasoline vapor.

### 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 gasoline is available. Where adequate information is not available, ATSDR, in conjunction with NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of gasoline.

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

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identified data needs will be evaluated and prioritized, and a substance-specific research agenda may be proposed.

### 5.7.1 Identification of Data Needs

**Physical and Chemical Properties.** The physical and chemical properties of gasoline and its primary component chemicals are well defined (Air Force 1989; ASTM 1989; OHM/TADS 1991; Sax and Lewis 1989) and can be used to estimate the fate of gasoline following release to the environment. Data needs associated with specific compounds that are components of the gasoline mixture (e.g., benzene, toluene, xylene, and other hydrocarbons and lead) are presented in the ATSDR toxicological profiles for these chemicals (ATSDR 1989, 1990, 1991). Therefore, no additional studies are needed at this time.

**Production, Import/Export, Use, and Release and Disposal.** Production, import/export, use, and release of gasoline are thoroughly described in the literature (see Chapter 4). Gasoline is used almost exclusively to fuel internal combustion engines (IARC 1989). The data indicate that the potential for human exposure is considerable and is most likely to occur from contact with contaminated air and/or groundwater. Production of gasoline has steadily increased between 1983 and 1989 from 277.2 million gallons/day to 306.6 million gallons/day (DOE 1989a). No data are available regarding predicted production volume of gasoline. Only limited information on one method of disposal (by spraying gasoline into an incinerator) was located (OHM/TADS 1991). No information regarding rules and regulations governing disposal of gasoline was located. More information on where and how gasoline is usually disposed of would aid in determining the potential risk of exposure to gasoline that has been improperly discarded.

**Environmental Fate.** Gasoline partitions to the different environmental compartments according to the physical/chemical properties of its individual components. The most important fate process is volatilization, especially for the short-chain alkanes (Air Force 1989; NESCAUM 1989). These compounds are transformed photochemically in the atmosphere (Cupitt 1980; Hendry and Kenley 1979; Stephens 1973). Migration to groundwater is also an important fate process for the soluble

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aromatics (Bouchard et al. 1990; DOI 1984; Yaniga 1984). The higher molecular weight hydrocarbons may sorb to soil (Air Force 1989; Hathaway and Andrews 1990). Gasoline-related hydrocarbons released to surface waters and soil are broken down by photooxidation and microbial degradation (Air Force 1989; Atlas 1981; Bossert and Bartha 1984; Thomas et al. 1990; Walker et al. 1975b). Biodegradation also occurs in groundwater (Wilson and McNabb 1983). The behavior of the gasoline mixture following release to the environment is well characterized. The fate of several of the most important component chemicals has also been studied (see ATSDR toxicological profiles for these chemicals [ATSDR 1989, 1990, 1991]). Data needs for specific hydrocarbons making up the gasoline mixture have been discussed in the ATSDR toxicological profiles for these chemicals (ATSDR 1989, 1990, 1991).

**Bioavailability from Environmental Media.** The various chemicals making up the gasoline mixture are known to be absorbed by inhalation, oral, and/or dermal routes. The extent of absorption by these routes will depend on the volatility, solubility, lipophilicity, and other properties of the specific components. Several of these component compounds have been discussed in detail in their individual ATSDR toxicological profiles (e.g., benzene, toluene, xylene, and lead), which should be consulted for further information (ATSDR 1989, 1990, 1991). More information linking exposure levels of gasoline and gasoline vapor 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 gasoline exposure.

**Food Chain Bioaccumulation.** Gasoline, as a mixture of hydrocarbons, does not bioaccumulate in the food chain per se. However, the individual components making up the mixture may bioaccumulate depending on their individual properties (Air Force 1989; NESCAUM 1989). In general, the alkenes (e.g., pentene, butene, hexene) will not tend to bioaccumulate, the aromatics have a moderate tendency to bioaccumulate, and the higher molecular weight alkanes will tend to bioaccumulate (Air Force 1989). The need for further research on biomagnification of the components of gasoline has been presented in the individual ATSDR toxicological profiles on these chemicals (ATSDR 1989, 1990, 1991). Research on the biomagnification of the gasoline mixture would not be useful since gasoline is

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not available to the food chain as a mixture because it partitions into its different constituent components as soon as it enters the environment. Individual components of the mixture may be bioconcentrated. Bioconcentration studies should be conducted on the individual components that are persistent and for which this information is lacking.

**Exposure Levels in Environmental Media.** There is a substantial amount of exposure data on air levels of gasoline vapors surrounding service stations and bulk loading terminals, and some data on air levels resulting from excavation and maintenance of underground storage tanks (ATSDR 1989, 1990, 1991). Reliable monitoring data for the levels of gasoline in contaminated media at hazardous waste sites would be useful so that the information obtained on levels of gasoline in the environment can be used, in combination with the known biomarkers used to identify exposure to gasoline, to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites.

**Exposure Levels in Humans.** Measurements of exposure levels have been taken for workers employed at service stations, bulk transfer facilities, and marine loading docks and those involved in storage tank excavation and maintenance (Halder et al. 1986a; Kearney and Dunham 1986; Kramer 1989; Shamsky and Samimi 1987). In addition, increased urinary excretion of phenol (20-40 mg/L) and lead (73.8 µg /L) and increased blood lead levels (256.3 µg /L) have been measured in workers occupationally exposed to gasoline (Moore et al. 1976; Rao et al. 1977; Turlakiewicz and Chmielnicka 1985), and increased levels of benzene have been measured in the expired air of service station workers (Brugnone et al. 1986). These increased levels are believed to result from the increased levels of lead and benzene absorbed when gasoline vapors are inhaled. However, because these and other chemicals in gasoline are frequently found in the environment, it is difficult to associate the increased levels of these chemicals specifically with exposure to gasoline. Methods more specific for gasoline exposure would aid in determining which markers would be most useful in determining exposure levels in humans. This information is necessary for assessing the need to conduct health studies on these populations.

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**Exposure Registries.** Service station workers, workers at bulk loading terminals and marine loading docks, and workers responsible for excavation and maintenance of gasoline storage tanks are known to have increased exposure to gasoline and its vapors. However, no registry exists for exposure to gasoline.

No exposure registries for gasoline 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 the exposure to this substance.

### 5.7.2 On-going Studies

A laboratory study on the effect of soil heterogeneity on the movement of light nonaqueous phase liquids is being conducted at the Colorado State University. The study, which is funded by the National Science Foundation, will utilize a dual energy gamma attenuation system to examine the movement of water, air, and light hydrocarbons through soils placed in a laboratory flume. Results of this research are expected to be useful for testing and validating models that predict the behavior of light hydrocarbons leaked from underground storage tanks to the water table.

Field and laboratory investigations being conducted by the U.S. Geological Survey of the Department of Interior are examining the anaerobic biodegradation of petroleum and gasoline hydrocarbons, including benzene and alkylbenzenes. A separate study is attempting to model the transport and biodegradation of organic mixtures, including gasoline.

At the University of Nevada, a study is underway that is attempting to: (1) establish improved methods for analyses of soils for gasoline constituents; and (2) determine the utility of using volatilization as a method for decontaminating soils containing gasoline. This field experiment will be conducted under conditions similar to those used in landfarming. The purpose is to demonstrate the relative rates of

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loss of various petroleum hydrocarbons, with identification of a treatment method that optimizes loss at lowest cost.

