

5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

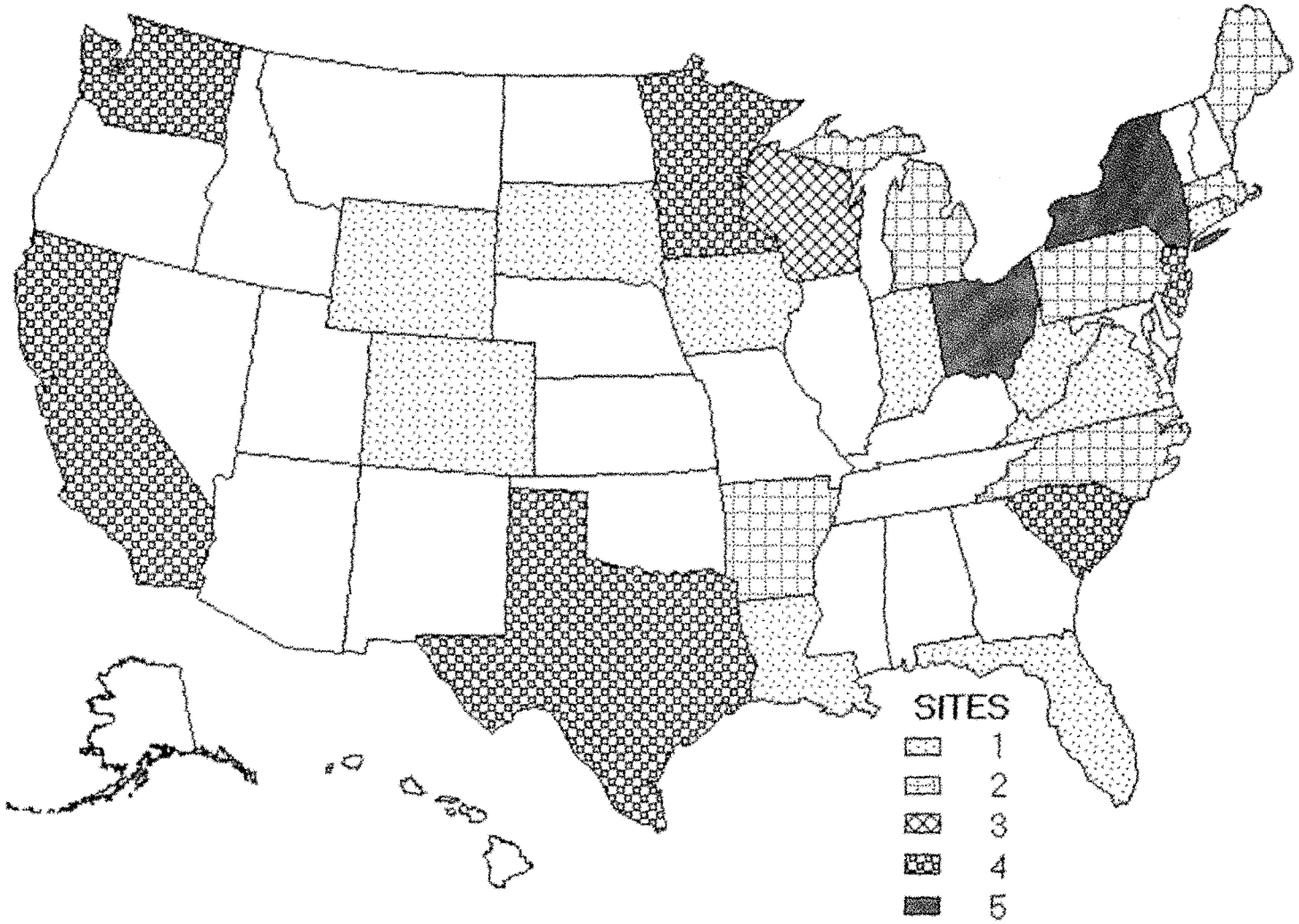
n-Hexane is a highly volatile component of the paraffin (also the alkane or aliphatic) fraction of crude oil and natural gas, and it is a constituent of heating and motor fuels refined from petroleum. Exposure from contact with vapors or emissions from these refined petroleum products is the most widespread form of low-level exposure for the general population. Most *n*-hexane in these fuels is oxidized (and therefore destroyed) as part of the combustion process to provide heat or drive internal combustion engines. Small amounts of *n*-hexane, along with other petroleum compounds, volatilize to the atmosphere during handling, storage in fuel tanks, or through incomplete combustion. Recent research (Ahearn et al.1996) suggests that certain fungi may be able to produce *n*-hexane. These fungi may be common in older buildings, and in some parts of the country may provide exposures from previously unsuspected indoor sources. *n*-Hexane is also produced as a relatively pure product for a number of specialized end uses, primarily as a solvent or as a component of certain glues and adhesives. Especially in urban areas, *n*-hexane may be a typical component of nonpoint source runoff when rainfall washes hydrocarbons deposited on roads and other surfaces into surface waters. Spills of refined petroleum products or of commercial *n*-hexane products may introduce *n*-hexane into soils or surface waters. Around urbanized areas, spill sites, refineries, tank storage facilities, underground storage tanks (e.g., at gas stations), or waste sites, can be sources of *n*-hexane subsequently transported into sediments or groundwater. Once introduced into deeper sediments or groundwater, *n*-hexane may be fairly persistent since its degradation by chemical hydrolysis is slow and opportunities for biodegradation may be limited under anoxic conditions or where nutrients such as nitrogen or phosphorus are in limited supply. In the atmosphere, the main degradation pathways involve destruction through the action of free radicals such as hydroxyl radicals.

n-Hexane has been identified in at least 60 of the 1,467 current or former EPA National Priorities List (NPL) hazardous waste sites (HazDat 1998). However, the number of sites evaluated for *n*-hexane is not known. The number of these sites within the United States can be seen in Figure 5-1.

5.2 RELEASES TO THE ENVIRONMENT

According to the Toxics Release Inventory (TRI), in 1996, a total of 70,685,942 pounds (32,062,933 kg) of *n*-hexane was released to the environment from 534 reporting facilities (TRI96 1998). Table 5-1 lists amounts released from these facilities. An estimated 77,303 pounds (35,064 kg) was released to publicly owned treatment works (POTWs), and an estimated 11,625,623 pounds (5,273,348 kg) were transferred

Figure 5-1. Frequency of NPL Sites with n-Hexane Contamination



Derived from HazDat 1998

Table 5-1. Releases to the Environment from Facilities That Manufacture or Process n-Hexane

Total of reported amounts released in pounds per year ^a								
STATE ^b	NUMBER OF FACILITIES	AIR ^c	WATER	LAND	UNDERGROUND INJECTION	POTW TRANSFER	OFF-SITE WASTE TRANSFER	TOTAL ENVIRONMENT ^d
AK	2	39,731	1	1,083	0	0	10	40,825
AL	15	1,570,973	0	0	0	100	97,240	1,668,313
AR	11	3,255,048	14,000	0	0	1,270	215	3,270,533
AZ	5	457,905	0	0	0	0	2,590	460,495
CA	40	1,114,984	0	0	0	250	144,952	1,260,186
CO	8	75,530	0	0	0	6	677,840	753,376
CT	4	122,187	5	0	0	1,300	99,225	222,717
DE	5	597,216	0	0	0	0	197,774	794,990
FL	8	253,743	0	0	0	755	115,998	370,496
GA	21	2,114,708	88	0	0	1,005	1,177,199	3,293,000
HI	2	31,493	250	500	0	0	755	32,998
IA	20	5,589,135	1,030	250	0	6,250	0	5,596,665
IL	39	10,331,776	1,847	659	0	14,852	196,088	10,545,222
IN	27	2,930,266	711	105	0	1,832	45,054	2,977,968
KS	10	2,165,816	11	0	0	1,077	291	2,167,195
KY	11	2,591,748	182	1,264	0	5	66,923	2,660,122
LA	40	4,216,364	3,393	11,026	101,329	11,000	1,301,515	5,644,627
MA	16	382,813	0	0	0	0	131,098	513,911
MD	3	358,760	0	0	0	5	1,761	360,526
ME	2	330,383	0	0	0	0	5,641	336,024
MI	28	713,270	0	0	250	2,430	4,928,420	5,644,370
MN	20	2,669,819	9	250	0	1,720	19,974	2,691,772
MO	17	2,733,991	0	0	0	1,255	57,656	2,792,902
MS	14	2,082,110	42,022	2	0	3	12,985	2,137,122
MT	6	413,150	6	255	0	0	0	413,411
NC	15	3,956,978	0	0	0	1,752	287,859	4,246,589
ND	4	510,343	0	0	0	6,267	0	516,610
NE	9	1,304,952	0	0	0	1,878	3,411	1,310,241
NJ	16	184,860	255	0	0	4	286,054	471,173
NM	4	133,844	0	0	0	0	300	134,144
NV	2	43,077	0	0	0	0	0	43,077
NY	7	38,759	0	0	0	0	30,128	68,887
OH	57	2,793,928	0	162	0	1,633	1,351,350	4,147,073
OK	9	942,993	33	84	0	250	827	944,187

Table 5-1. Releases to the Environment from Facilities That Manufacture or Process n-Hexane (continued)

Total of reported amounts released in pounds per year ^a								
STATE ^b	NUMBER OF FACILITIES	AIR ^c	WATER	LAND	UNDERGROUND INJECTION	POTW TRANSFER	OFF-SITE WASTE TRANSFER	TOTAL ENVIRONMENT ^d
OR	1	28,631	0	0	0	478	159	29,268
PA	20	486,136	258	35	0	26	286,345	772,800
PR	15	271,021	151,133	0	0	14,900	62,885	499,939
RI	1	4	0	0	0	0	0	4
SC	11	811,042	541	500	0	5,000	35,101	852,184
SD	2	280,000	0	0	0	0	4,469	284,469
TN	18	2,197,647	0	0	0	2,006	223,040	2,422,693
TX	121	9,726,651	1,779	6,429	0	6,818	16,968,300	26,709,977
UT	10	97,391	0	321	0	0	5	97,717
VA	16	964,473	0	0	0	750	215,848	1,181,071
VI	1	180,829	72	0	0	0	0	180,901
WA	9	273,954	559	6	0	5	5,805	280,329
WI	10	118,443	0	0	0	15	37,713	156,171
WV	5	52,711	0	0	0	0	28,901	81,612
WY	5	168,321	10	975	0	0	243	169,549

Source: TRI96 1998

^a Data in TRI are maximum amounts released by each facility^b Post office state abbreviations used^c The sum of fugitive and stack releases are included in releases to air by a given facility^d The sum of all releases of the chemical to air, land, and water, and underground injection wells; and transfers off-site by a given facility

POTW = publicly owned treatment works

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offsite (TRI96 1998). The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

Since *n*-hexane is a component of refined petroleum products, there is considerable potential for releases to environmental media through the use of heating and motor fuels. Table 5-2 summarizes the uses of petroleum products according to major demand categories (e.g., “transportation”) and displays estimated use levels in barrels (and liter equivalents) and by percentages for the various end-use demands for specific fuel types (e.g., kerosene or fuel oil). While *n*-hexane can be a minor constituent (less than 1% by weight) of several of these petroleum products, its physical properties as a light alkane make it most suitable for use in gasoline. Approximately 98% of the demand for gasoline involves transportation, mainly cars and trucks. The composition of gasolines has changed over the years, mainly in an effort to maintain the so called octane ratings of the fuels. Since the 1980s the growing use of nonleaded gasolines has led to a growing percentage of high-octane benzene and toluene in gasoline blends. For modern gasoline mixtures, the total percentage by weight of the *n*-hexane component is approximately 3% (Brugnone et al.1991; Heath et al.1993; Stelljes and Watkin 1993). Of the 2,608 million barrels of motor gasoline consumed for transportation in 1992 (designated “transportation” in Table 5-2) about 27,300 million pounds (12,409 million kg) are from the *n*-hexane fraction (PennWell 1994; Stevens 1988). This figure is about 76 times the 358 million pounds (143 million kg) of commercial *n*-hexane produced annually in the 1970s (Marks et al.1980). Most gasoline, along with its *n*-hexane fraction, is consumed during its combustion in motor cars and other engines. However, gasoline use results in a variety of emission losses from refueling, evaporation while gasoline is stored in fuel tanks or ignition systems, and exhaust releases when there is incomplete combustion of fuels (EPA 1994h). EPA only tracks trends in total hydrocarbon or total volatile organic compound (VOC) emissions, so that quantitative estimates for the *n*-hexane released from automobiles and trucks are not available. Assuming that only 1% of the *n*-hexane of motor fuels is released to environmental media, such releases could be on the same order of magnitude as the total amount of relatively pure *n*-hexane associated with the major end-uses described in Chapter 4. In addition to emissions to the atmosphere, releases from heating and motor fuel uses to other environmental media are possible as a result of leaks and spills at refineries, pipelines, large tank batteries (or tank “farms”), above- and below-ground storage tanks, tanker trucks and railroad tanker cars, or from minor releases at garages or around homes and workplaces. Crude oil spills also result in the release of *n*-hexane to the air or other environmental media.

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Table 5-2. Demand Patterns for Major Petroleum Products (1992)^a

Product	Residential	Commercial	Industrial	Transportation	Electric utilities	Total
Motor gasoline ^b	0 (0.0) 0	15 (<1.0) 2,385	37 (1.4) 5,883	2608 (98.0) 414,672	0 (0.0) 0	2,660
Kerosene	11 (73.3) 1,749	2 (13.3) 318	2 (13.3) 318	0 (0.0) 0	0 (0.0) 0	15
Distillate fuel oil	148 (13.6) 23,532	80 (7.3) 12,720	196 (18.0) 31,164	654 (60.0) 103,986	12 (1.1) 1,908	1,090
Residual fuel oil	0 (0.0) 0	30 (7.5) 4,770	62 (15.5) 9,858	172 (42.9) 27,348	136 (33.9) 21,942	400
Liquid petroleum gas and ethanes	106 (16.5) 16,858	19 (3.0) 3,021	513 (79.9) 81,567	5 (0.8) 795	0 (0.0) 0	643

^a Top line: millions of barrels (% of total sectoral demand)
Bottom line: millions of liters

^b Typically contains >1% *n*-hexane

Note: 1 barrel = 42 U.S. gallons = 159 liters

Source: PennWell 1994

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In addition to releases associated with the ordinary use of refined petroleum products as a fuel, ongoing research (Ahearn et al. 1996) suggests that a variety of fungi found in ducts and insulation materials in homes or office buildings are capable of releasing gases that include *n*-hexane.

Where the buildings have poor ventilation properties, commonly referred to as “sick-building syndrome” (Sundell 1996), the indoor air releases of *n*-hexane may sometimes be sufficient to pose public health concerns. *n*-Hexane is also among the various off-gassing constituents encountered at sanitary landfills (Brosseau and Heitz 1994; O’Leary and Walsh 1995). There is also evidence (McKay et al. 1996) that marine phytoplankton produce a variety of non-methane hydrocarbons, including small amounts of *n*-hexane, from the metabolism of polyunsaturated lipids in dissolved organic materials. Very small amounts of *n*-hexane may also be among the biogenic emissions from different types of terrestrial vegetation (Isidorov et al. 1985; Winer et al. 1992).

5.2.1 Air

According to the Toxics Release Inventory (TRI), in 1996, the estimated releases of *n*-hexane of 58,649,487 pounds (26,603,233 kg) to air from 534 reporting facilities accounted for about 82.9% of total environmental releases (TRI96 1998). Table 5-1 lists amounts released from these facilities. The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

Most releases of *n*-hexane to environmental media are to air. Based on its Henry’s law constant, *n*-hexane discharged to water will volatilize rapidly; however, the amount volatilized will vary depending on a number of factors including the temperature, turbulence, and depth of the receiving water. *n*-Hexane spilled onto surface soils will also volatilize to the air. Data sources were not identified allowing comprehensive quantitative estimates of the amount of *n*-hexane released on an annual basis to the air. In addition to releases from such commercial applications as edible oil extraction, the other major sources of atmospheric releases would be from emissions related to the *n*-hexane contained in heating and motor fuels.

n-Hexane was identified in air samples collected at 17 of the 60 NPL hazardous waste sites where it had been detected (HazDat 1998).

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5.2.2 Water

According to the Toxics Release Inventory (TRI), in 1996, the estimated releases of *n*-hexane of 215,775 pounds (97,875 kg) to water from reporting facilities accounted for less than 1 percent of total environmental releases (TRI96 1998). Table 5-1 lists amounts released from these facilities. The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

n-Hexane is probably released to water from a number of sources including industrial discharges, effluents from municipal waste-treatment plants, and nonpoint-source runoff from roads and other surfaces. Insufficient information is available to quantify the releases in a comprehensive fashion.

n-Hexane was identified in surface water at one site and in groundwater at 20 sites among the 60 NPL hazardous waste sites where it had been detected (HazDat 1998).

5.2.3 Soil

According to the Toxics Release Inventory (TRI), in 1996, the estimated releases of *n*-hexane of 16,175 pounds (7,337 kg) to soil from reporting facilities accounted for less than 1 percent of total environmental releases (TRI96 1998). Table 5-1 lists amounts released from these facilities. The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

n-Hexane is probably released to soil or sediments from spills and during the landfilling of sludges and other wastes generated from industrial processes and municipal sewage treatment; however, no specific quantitative information concerning release levels for *n*-hexane-containing wastes was located in the literature.

n-Hexane has been identified in soil samples collected at 14 and sediment samples collected at two of the 60 NPL hazardous waste sites where it was detected in some environmental media (HazDat 1998).

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5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

The physical properties of *n*-hexane (see Table 3-2) that affect its transport and partitioning in the environment are: water solubility of 9.5 mg/L; $\log[K_{ow}]$ (octanol/water partition coefficient), estimated as 3.29; Henry's law constant, 1.69 atm-m³ mol; vapor pressure, 150 mm Hg at 25 °C; and $\log[K_{oc}]$ in the range of 2.90 to 3.61. As with many alkanes, experimental methods for the estimation of the K_{oc} parameter are lacking, so that estimates must be made based on theoretical considerations (Montgomery 1991).

The dominant transport process from water is volatilization. Based on mathematical models developed by the EPA, the half-life for *n*-hexane in bodies of water with any degree of turbulent mixing (e.g., rivers) would be less than 3 hours. For standing bodies of water (e.g., small ponds), a half-life no longer than one week (6.8 days) is estimated (ASTER 1995; EPA 1987a). Based on the log octanol/water partition coefficient (i.e., $\log[K_{oc}]$) and the estimated log sorption coefficient (i.e., $\log[K_{oc}]$) (see Table 3-2) *n*-hexane is not expected to become concentrated in biota (Swann et al.1983). A calculated bioconcentration factor (BCF) of 453 for a fathead minnow (ASTER 1995) further suggests a low potential for *n*-hexane to bioconcentrate or bioaccumulate in trophic food chains.

In soil, the dominant transport mechanism for *n*-hexane present near the surface probably is volatilization (based on its Henry's law constant, water solubility, vapor pressure, and K_{oc}), but no experimental information focusing directly on *n*-hexane was found to confirm this assumption. While its estimated K_{oc} values suggest a moderate ability to sorb to soil particles, *n*-hexane has a density (0.6603 g/mL at 20 °C) well below that of water and a very low water solubility of 9.5 mg/L. *n*-Hexane would, therefore, be viewed as a light nonaqueous phase liquid (LNAPL), which would suggest a low potential for leaching into the lower soil depths since the *n*-hexane would tend to float on the top of the saturated zone of the water table (Feenstra et al.1991; Hunt et al.1988). Unless present in deeper soil layers (which can sometimes happen at waste sites or with underground storage tank leaks), *n*-hexane would generally stay near the soil surface and, if not appreciably sorbed into the soil matrix, would be expected eventually to volatilize to the atmosphere. Exceptions would involve locations with shallow groundwater tables where there were large spills of hexane products. In such cases, the *n*-hexane could spread out to contaminant a large volume of soil materials.

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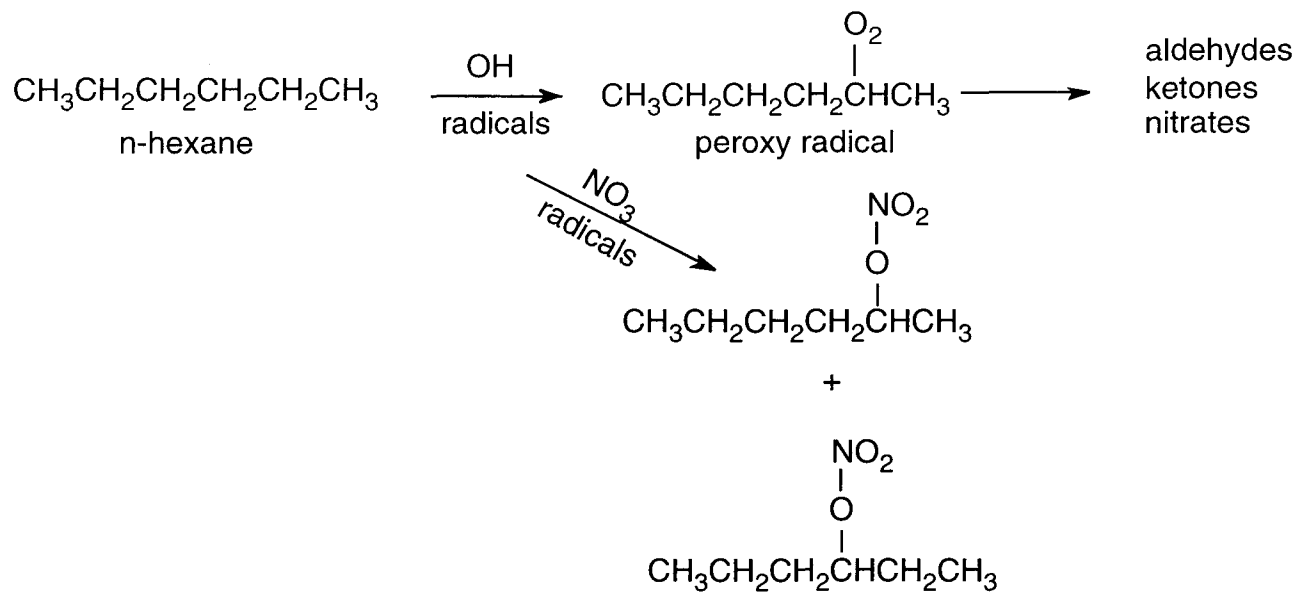
5.3.2 Transformation and Degradation**5.3.2.1 Air**

n-Hexane does not absorb ultraviolet (UV) light at 290 nm and is thus not expected to undergo direct photolysis reactions. The dominant tropospheric removal mechanism for *n*-hexane is generally regarded to be decomposition by hydroxyl radicals (Atkinson and Carter 1984; Atkinson et al.1982). Calculations assuming typical hydroxyl radical concentrations suggest a half-life of approximately 2.9 days (SRC 1994b). While *n*-hexane can react with nitrogen oxides to produce ozone precursors under controlled laboratory conditions (Montgomery 1991), the smog-producing potential of *n*-hexane is very low compared to that of other alkanes or chlorinated VOCs (Kopczynski et al.1972). Hydroxyl ion reactions in the upper troposphere, therefore, are probably the primary mechanisms for *n*-hexane degradation in the atmosphere. As with most alkanes, *n*-hexane is resistant to hydrolysis (ASTER 1995; Lyman et al.1982). The proposed decomposition of *n*-hexane in air is shown in Figure 5-2.

5.3.2.2 Water

Although few data are available dealing explicitly with the biodegradation of *n*-hexane in water, neither hydrolysis nor biodegradation in surface waters appears to be rapid compared with volatilization. In surface waters, as in the atmosphere, alkanes such as *n*-hexane would be resistant to hydrolysis (ASTER 1995; Lyman et al.1982). Biodegradation is probably the most significant degradation mechanism in groundwater. One study was identified (McClay et al.1995) that documented the ability of *Pseudomonas mendocina* bacteria to metabolize *n*-hexane in laboratory microcosms simulating groundwater conditions. Mixed bacterial cultures as well as pure cultures are documented as capable of metabolizing *n*-hexane under aerobic conditions (Heringa et al.1961; Rosenberg et al.1992). A study of a biofiltration system to remove VOCs from air used a sludge-like composting biofiltering system that was effective in causing the biodegradation of *n*-hexane (Morgenroth et al.1996); this study involved a special composting system to allow the introduction of nitrogen fertilizers to overcome a nutrient limitation. Most of the available literature deals with petroleum mixtures containing several types of alkanes. In general, linear alkanes (such as *n*-hexane) are viewed as the most readily biodegradable fractions in petroleum (Leahy and Colwell 1990), particularly when oxygen is present in solution.

Figure 5-2. Degradation of *n*-Hexane in Air by Free Radicals



Source: Atkinson 1985

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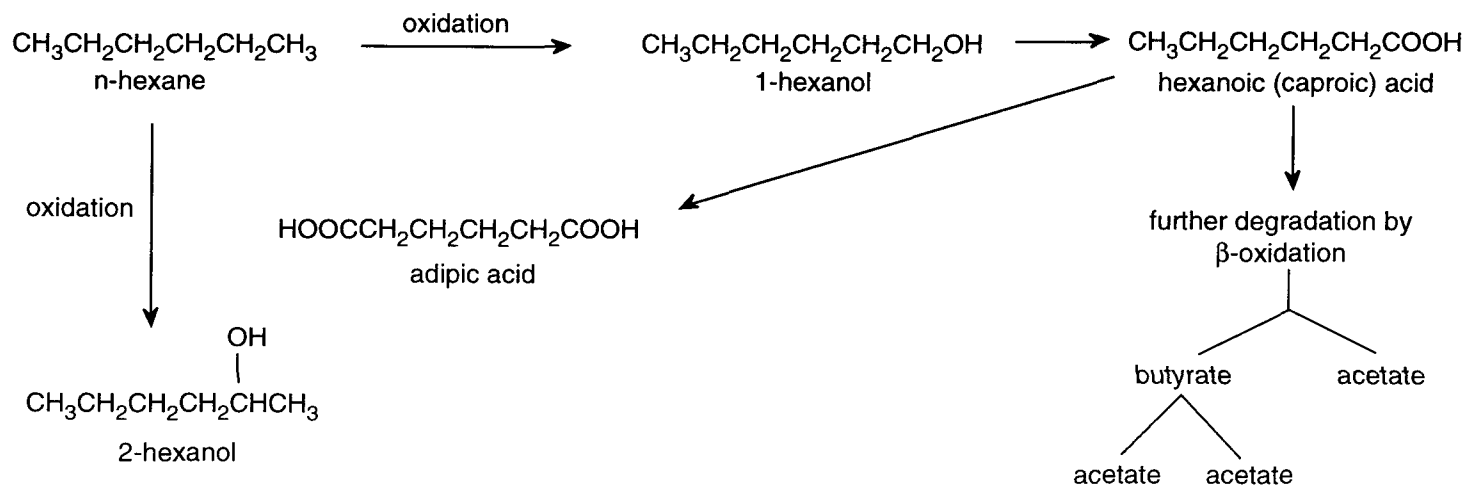
Since *n*-hexane is highly volatile, it is often excluded from the list of constituents included in studies on biodegradation or bioremediation of petroleum wastes or in studies of surface waters receiving pollutant loads from runoff or discharges. Attention is generally focused on complex mixtures of hydrocarbons, starting with fractions heavier or less volatile (usually C10 or longer chain alkanes, aromatics such as benzene or toluene, and PAHs (polyaromatic hydrocarbons)) than the lighter constituents of gasoline (Crawford et al.1995; Latimer et al.1990; Rosenberg et al.1992; Sauer et al.1993; Shaw et al.1986). Once introduced into groundwater, *n*-hexane may be fairly persistent since its degradation by chemical hydrolysis is slow and opportunities for biodegradation may be limited under anoxic conditions or where nutrients such as nitrogen or phosphorus are in limited supply.

5.3.2.3 Sediment and Soil

The findings presented above in Section 5.3.2.2 on bioremediation in groundwater are relevant for many soil and sediment systems. Figure 5-3 outlines the probable biodegradation of *n*-hexane based on metabolites isolated from a pure culture of *Pseudomonas* (Heringa et al.1961). The most important biodegradation processes involve the conversion of the *n*-hexane to primary alcohols, aldehydes and, ultimately, into fatty acids. Similar processes are encountered with other light hydrocarbons such as heptane. In general, unless the *n*-hexane is buried at some depth within a soil or sediment, volatilization is generally assumed to occur at a much more rapid rate than chemical or biochemical degradation processes. Once introduced into deeper sediments, *n*-hexane may be fairly persistent since its degradation by chemical hydrolysis is slow and opportunities for biodegradation may be limited under anoxic conditions or where nutrients such as nitrogen or phosphorus are in limited supply.

5. 4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

The widespread use of *n*-hexane as an extractant in the laboratory creates problems in interpreting concentration readings at low levels. Even with good quality control, it may often be impossible to determine whether to attribute a measured value to the actual levels in a sample or to contamination from *n*-hexane in the laboratory environment (Otson et al.1994). For the most part, *n*-hexane is not a common target analyte from water or soil samples. While data based on ambient air samples or sampling in the air of various workplace or residential environments are more numerous, most EPA regulatory programs rely on bulk measurements of total hydrocarbons or total volatile compounds rather than on measurements of specific compounds such as *n*-hexane (Bishop et al.1994; DeLuchi 1993).

Figure 5-3. Aerobic Biodegradation of *n*-Hexane in Sediment and Soil

Source: Heringa et al. 1961

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5.4.1 Air

Concentrations of *n*-hexane in the air can be expressed as parts per million by volume (ppmv) or as mg/m³. For *n*-hexane, 1 ppmv = 3.52 mg/m³, and for lower concentrations, 1 part per billion volumetric (ppbv) = 3.52 µg/m³ (HSDB 1996). *n*-Hexane is found at low levels in both rural and urban ambient air, with concentrations generally well below 50 ppbv for ambient air. In remote sites, readings of less than 0.5 ppbv are typical. A study of four rural sites in southern Canada showed median ambient air concentrations of *n*-hexane in the range of 0.01 to 0.12 ppbv (Bottenheim and Shepherd 1995). Higher levels can be encountered in urban areas, largely due to emissions from automobile exhaust. In the polluted atmosphere of the Los Angeles central business district, ambient air concentrations as high as 25 ppbv were documented in the 1960s (Neligan 1962); these levels are very similar to the concentrations of *n*-hexane measured in automobile exhaust collected during the same time period. Samples from Los Angeles in 1968 showed *n*-hexane levels of 82 ppbv (Kopczynski et al. 1972). With progressive improvements in emission controls, the levels of many air pollutants in urbanized areas today are generally far lower. A recent study of average VOC concentrations in the ambient air of several large cities showed the following results for *n*-hexane: Vienna 2.2 ppbv; Hamburg 3.8 ppbv; Sydney 2.1 ppbv; Chicago 2.0 ppbv; Osaka 5.5 ppbv; and Athens 1.6 ppbv (Moschonas and Glavas 1996). Air samples from Kuwaiti houses after the Gulf War (which introduced large amounts of air pollutants from burning oil) showed average *n*-hexane levels of only 4.4 ppbv (Bouhamra 1995).

n-Hexane may be expected to comprise around 2% of the VOCs in urban air polluted with hydrocarbons from automobile emissions or other combustion byproducts (Barrefors and Petersson 1993). The *n*-hexane concentrations in urban air will typically be approximately 60% of the concentrations of benzene (Daisey et al. 1994). Close proximity to the exhaust systems of cars or other gasoline-powered vehicles can lead to exposures to increased concentrations of *n*-hexane. Under rush-hour conditions, the concentrations in the interior air of buses will tend to be lower (55 µg/m³ or 19.8 ppbv) than the interior levels in cars (69 µg/m³ or 24.9 ppbv) or the air around persons riding motorcycles (106 µg/m³ or 38.1 ppbv) (Chan et al. 1994). Transportation tunnels may contain hydrocarbon concentrations around six times the levels encountered with ordinary open-air vehicular traffic; this is probably associated with similarly elevated levels of *n*-hexane (Barrefors and Petersson 1993). Measurements of hydrocarbons from vehicular exhaust at the Fort McHenry Tunnel in Baltimore, Maryland, have shown *n*-hexane levels just under 60 ppbv (Zielinska et al. 1996). *n*-Hexane does not seem to be present in tobacco smoke, although such smoke can lead to elevations in the concentrations of other hydrocarbons in the air of interior rooms (Barrefors and Petersson

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1993). A complication in such testing is that hydrocarbons in the smoke may have been introduced from sources such as polluted urban air or *n*-hexane from cigarette lighters. The air in well ventilated office buildings in urban areas of California contained *n*-hexane levels of approximately $0.55 \mu\text{g}/\text{m}^3$ (1.5 ppbv) (Daisey et al.1994). Other studies of heavily polluted urban areas have suggested that the air in offices will have *n*-hexane levels at least an order of magnitude lower than the peak levels in rush-hour traffic in cars or other vehicles (Chan et al.1994); the same studies showing that the median concentrations averaged over an entire commuting trip are about the same as for the time-averaged median concentrations of *n*-hexane in office buildings ($<9 \mu\text{g}/\text{m}^3$ or <3.2 ppbv).

Recent research suggests that gases released by various fungi in ductwork, inner walls, and crawl spaces contain a variety of VOCs, including *n*-hexane (Ahearn et al.1996). Of the total levels of VOCs measured *in situ* from fungal-colonized insulation materials in a 2-year-old office building, *n*-hexane comprised about 2.69% of the total measured VOCs; in air samples collected under laboratory conditions using cultures prepared from fungal isolates, the *n*-hexane contribution to the total measured VOCs was 4.85% (Ahearn et al.1996). Measurements of the interior air of an office building located in the Houston area showed total VOC concentrations (expressed as carbon) in excess of 100 ppbv. The VOCs levels included detectable amounts of *n*-hexane as well as toluene and benzene (Ahearn et al.1996).

Concentrations in some workplace settings may be higher than typical ambient air levels. Samples collected in tire factories during the 1970s showed median *n*-hexane levels of 25.9 ppmv around the work area where the rubber curing took place (Van Ert et al.1980). When workers have assembled items in poorly ventilated rooms, *n*-hexane levels ranging from 500 to 2,500 ppmv have been documented (Iida 1982). Similar workplace findings, usually in countries other than the United States, have been documented, with *n*-hexane concentrations in workspace air in excess of 500 ppmv (Graham et al.1995). Elevated levels in air are also found in substance abuse cases, where pure *n*-hexane or mixtures containing significant amounts of *n*-hexane are used to produce a "high" (Altenkirch et al.1977; Graham et al.1995).

n-Hexane is a common trace component in landfill gases at many waste sites (Brosseau and Heitz 1994; O'Leary and Walsh 1995). The *n*-hexane concentrations of these emissions have been documented to range from 3 to $10 \text{ mg}/\text{m}^3$ (1.1-3.6 or 1,100-3,600 ppbv). While these levels would be expected to decrease rapidly as the landfill gases were dispersed into the ambient air, areas near the ground or pockets of air in trenches or excavations could reach levels significantly above the concentrations normally encountered in ambient air. For instance, data averaged over 15-minute intervals during site remediation

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work at a reclaimed oil refinery site showed levels as high as 121.51 mg/m³ (43.70 ppmv) in the air around a backhoe digging trench in the petroleum-contaminated soils (Verma et al.1992). Samples from the same study averaged over a typical 8-hour workshift for the area around the backhoe showed average levels of 3.06 mg/m³ (1.10 ppmv). Even higher levels (perhaps in excess of 10,000 ppmv) are possible around large spills of *n*-hexane; at such elevated concentrations, as with many components of gasoline-type hydrocarbons, there could be considerable danger from explosions, which are possible when the *n*-hexane levels exceed approximately 1.2% of the volume of air (Merck 1989). Since 0.1% by volume is equivalent to 1,000 ppmv, this flash-point level for *n*-hexane would be at a level of 12,000 ppmv or higher.

5.4.2 Water

In general, data on levels in water or groundwater are very limited, with no information being identified in the literature. Information on levels in public water supplies was not identified. Since *n*-hexane is highly volatile, typical treatment techniques for drinking water supplies in larger towns and cities would be expected to volatilize the *n*-hexane before it could enter the distribution system. It is likely that some *n*-hexane would be found in groundwater contaminated by gasoline leaks from underground storage tanks (UST). This could be a matter of concern for some domestic groundwater wells used for drinking water supplies. Since the emphasis in UST programs is usually on the more soluble aromatic fractions (e.g., benzene) or on bulk measurements of total petroleum hydrocarbons (TPH) (Potter 1993), no information could be identified in the literature dealing explicitly with *n*-hexane.

5.4.3 Sediment and Soil

Very little information could be identified dealing with *n*-hexane levels in sediments and soils. *n*-Hexane has been identified among the contaminants in an offsite oilfield-disposal pit in New Mexico (Eiceman et al. 1986). Since *n*-hexane is a trace constituent of crude oil and natural gas, as well as a component of refined petroleum products, soil or sediment contamination with *n*-hexane can be expected near oilfield production sites, large soil spills, slush pits and other areas around refineries, and in waste sites where petroleum products or other *n*-hexane-containing wastes had been disposed. Detections would also be likely near many tank storage facilities, pipelines, truck or rail transfer sites, car repair facilities, automobile assembly or storage facilities, and auto and truck fueling facilities (DeLuchi 1993).

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At many waste sites, *n*-hexane has been detected in the landfill gases vented from the soils at the disposal sites (Brosseau and Heitz 1994; O'Leary and Walsh 1995). While information in the literature is extremely limited, trace levels of *n*-hexane are probably found in the soils or the soil gases at many waste disposal sites. *n*-Hexane has been identified in the soil at 14 sites and in sediments at two sites among the 60 NPL hazardous waste sites where it was detected in some environmental medium (HazDat 1998).

5.4.4 Other Environmental Media

n-Hexane is exempted from analysis of most foodstuffs (the exceptions are spice oleoresins and corn endosperm oil) or as an inert ingredient in pesticide formulations (see Chapter 4; Firestone 1997). Testing for alkanes is often directed at compounds less volatile (e.g., C10 or higher) than *n*-hexane (Hernandez et al. 1995). There is, therefore, limited information in the literature on the levels of *n*-hexane encountered in foodstuffs. Analyses carried out in the 1960s and 1970s would have sometimes involved analytical methods not considered accurate by contemporary standards. Caution is also needed in interpreting published results to make sure the testing did not involve materials that had not yet gone through the complete cycle of solvent recovery, heating, and final vacuum treatment to recover the *n*-hexane solvent and remove as much as possible of this hydrocarbon from the final product intended for human consumption. Before these recovery processes, the crude oil or meal products can be expected to show appreciably high levels of *n*-hexane. In studies of fully processed edible oil products carried out in the 1960s it was determined that *n*-hexane residues were generally at levels below 10 ppm (Watts and Holswade 1967). Recent investigations using more precise modern analysis techniques (Hautfenne et al. 1987) concluded that residual *n*-hexane residues for refined food products would be less than 2 ppm. If the standard assumption of 80 g of fat consumed per 70-kg person per day is made, such residual levels would be the equivalent of no more than 2.29 µg/kg/day of *n*-hexane, which is a toxicologically insignificant amount.

No recent studies could be identified that were performed in the United States on levels in expired air. A study of hydrocarbon contents in expired air in the Chicago area carried out in the late 1970s found average *n*-hexane concentrations from 54 human volunteers breathing urban air to be approximately 4.7 ng/L (Krotoszynski et al. 1979). Most studies of *n*-hexane have involved occupational exposures, especially in shoe or sandal factories, in Japan or Italy. Since *n*-hexane is rapidly metabolized by humans to such compounds as 2,5-hexanedione, investigations of toxic substances in blood or urine typically focus on these metabolites (Mutti et al. 1993; van Engelen et al. 1995). In one study of shoe assembly workers in

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Italy, blood and urine levels of *n*-hexane were taken concurrently with readings of the *n*-hexane in workplace air and alveolar air. The median concentration for workplace (environmental air) was 87 ng/L; for alveolar air the median level was 26 ng/L; for blood samples the median concentration was 365 ng/L; and for urine samples the median was 549 ng/L (Brugnone et al.1991). Enough information has been assembled from ongoing studies from Italy (Brugnone et al.1994) to estimate typical levels in blood and urine from people in the general population living in rural areas as opposed to urban areas. For urine samples, the median value for the general population sampled in the rural areas was 401 ng/L; the median value for the urban areas was slightly higher at 550 ng/L; and the combined rural and urban median level was 492 ng/L (range, 24 to 1,608 ng/L). For blood samples, the rural median levels were 260 ng/L, and the urban general population levels were 287 ng/L. Special concomitant sampling for blood levels was also carried out for chemical plant workers, for whom the median blood levels were 729 ng/L. The pooled median blood levels (general rural population, plus general urban population, plus urban chemical workers) was 293 ng/L (range, 25 to 8,058 ng/L). In some workplace settings, median 8-hour-workshift levels in the air for *n*-hexane of 415 mg/m³ (1,154 ppmv) have been documented (Mutti et al.1993). In one study in the areas around Bayonne, New Jersey; Jersey City, New Jersey; Bridgeville, Pennsylvania; and Baton Rouge, Louisiana, *n*-hexane was detected (no concentrations reported) in samples of human breast milk (Pellizzari et al.1982).

n-Hexane is contained in a variety of products commonly used in household settings. Given its volatility, this creates possibilities for exposures from inhalation as well as by dermal contact and ingestion. In a study of over 1,000 common household products, *n*-hexane was detected in 101 products, about the same detection rate as for BTEX compounds (e.g., benzene, toluene, xylene or ethylbenzene) and other normal alkanes. *n*-Hexane was detected in more than 10% of the items sampled in the following product categories: automotive products; oils, greases and lubricants; and adhesive-related products (Sack et al. 1992).

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Low-level exposures to *n*-hexane can possibly occur for much of the United States population, especially those that live in urban areas or those that commute in areas with heavy traffic, due to emissions of *n*-hexane associated with motor fuel use. As such, the general population will be exposed to very low levels at all times, while those living in urban centers may be exposed to slightly higher levels.

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Current empirically based estimates of exposures to *n*-hexane in various occupations are lacking. Some insights can be gleaned from the National Institute for Occupational Safety and Health's (NIOSH) National Occupational Hazard Survey (NOHS), a database (the NOHS database is also called the National Occupational Exposure Survey or NOES database) that estimates potentially exposed workers in a variety of manufacturing jobs (Sieber et al. 1991). Based on conditions typical of the mid-1970s it was estimated that 643,120 workers had potential exposures to *n*-hexane (NOES 1991). Occupations with 5,000 or more workers with potential exposure risks included the following: shoe and footwear assembly workers; hospital staff and laboratory technicians; workers operating or repairing typesetting and printing machinery; construction workers, carpet layers and carpenters; auto mechanics; workers in plants manufacturing tires or inner tubes; and workers in air transport and air-freight operations. The NOES database covers only certain manufacturing sector occupations and does not include workers at edible-oil extraction facilities, who are usually classified as agricultural workers.

5.6 EXPOSURES OF CHILDREN

This section focuses on exposures from conception to maturity at 18 years in humans and briefly considers potential pre-conception exposure to germ cells. Differences from adults in susceptibility to hazardous substances are discussed in Section 2.6, Children's Susceptibility.

Children are not small adults. A child's exposure may differ from an adult's exposure in many ways. Children drink more fluids, eat more food, and breathe more air per kilogram of body weight, and have a larger skin surface in proportion to their body volume. A child's diet often differs from that of adults. The developing human's source of nutrition changes with age: from placental nourishment to breast milk or formula to the diet of older children who eat more of certain types of foods than adults. A child's behavior and lifestyle also influence exposure. Children crawl on the floor; they put things in their mouths; they may ingest inappropriate things such as dirt or paint chips; they spend more time outdoors. Children also are closer to the ground, and they do not have the judgement of adults in avoiding hazards (NRC 1993).

Children, like adults, are subject to low level *n*-hexane background exposures associated with emissions from the combustion of motor fuels or heating oil or other uses of petroleum products. Some products used in the home, such as rubber cement, contain *n*-hexane and could pose exposure risks to children from inhalation. In addition to inhalation exposures through the normal use of such products in poorly ventilated interior areas, children may engage in "glue sniffing" substance-abuse behaviors that could pose serious

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inhalation exposure risks. Dermal exposures are also possible from hexane-containing household products. For very small children, accidental ingestion of hexane-containing materials is also a potential exposure risk. Other potential exposures are possible from hazardous waste sites. There have been no documented secondary or take-home exposures for children from materials transferred from the parents' workplace on clothes, skin, hair, tools, or other objects (NIOSH 1995). Such exposure risks are not expected to be a concern with *n*-hexane because it is highly volatile.

Although concentration levels were not reported, studies have shown detections of *n*-hexane in human breast milk (Pellizzari et al.1982). In chapter 2, the discussion of PBPK modeling suggests the likelihood for breast milk transfers to nursing infants. No studies were identified dealing with levels of *n*-hexane in amniotic fluid, meconium, cord blood, or neonatal blood that would document prenatal exposures. There are no studies dealing with exposure or body burden measurements on children. Given the absence of such studies targeted at children, it is unknown whether children are different in their weight-adjusted intake responses to *n*-hexane.

5.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

In addition to individuals who are occupationally exposed to *n*-hexane (see Section 5.5), there are several groups within the general population that have potentially high exposures (higher than background levels) to *n*-hexane. These populations include individuals living in proximity to sites where *n*-hexane is produced or sites where *n*-hexane is disposed, and individuals living near the 60 NPL hazardous waste sites where *n*-hexane has been detected in some environmental media (HazDat 1998). Work situations where *n*-hexane is used as a solvent or in adhesives and where there are very poor ventilation conditions could also involve elevated exposure risks. Workers in poorly ventilated confined areas (e.g., warehouses, garages, tunnels) or trenches where *n*-hexane levels could build up from engine exhaust or from off-gassing, as in some landfill sites, might also experience higher exposures.

Workers in tire-manufacturing facilities may have a heightened potential for health hazards since the rubber vulcanization process can involve exposures to *n*-hexane (Graham et al.1995).

Individuals who subject themselves to substance abuse by inhaling *n*-hexane or vapors from products containing significant levels of *n*-hexane would also experience potentially high exposure levels (Altenkirch et al.1982; Graham et al.1995).

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5.8 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 *n*-hexane 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 *n*-hexane.

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.

5.8.1 Identification of Data Needs

Physical and Chemical Properties. Data on physical and chemical properties are essential for estimating the partitioning of a chemical in the environment. The data on known physical and chemical properties form the basis of many of the input requirements for environmental models that predict the behavior of a chemical under specific conditions including those in hazardous waste landfills. Most of the necessary data on physical and chemical properties are available for *n*-hexane.

Production, Import/Export, Use, Release, and Disposal. Production methods for *n*-hexane are described in the literature, and there does not appear to be a need for further information. Uses of *n*-hexane are documented, although a detailed description of all uses is not available. Quantitative estimates of production levels for the more highly purified forms of *n*-hexane are available. The amounts of *n*-hexane associated with many types of motor and heating fuels can only be roughly estimated. Information on import and export levels is lacking. This information would be useful for estimating the potential for environmental releases from manufacturing and use industries as well as the potential environmental burden. However, it is difficult to obtain this information in the detail desired since it is generally considered to be confidential business information for those industries that manufacture *n*-hexane. Information on disposal practices is limited.

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According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit chemical release and off-site transfer information to the EPA. The Toxics Release Inventory (TRI) contains this information. This database will be updated yearly and provides a list of industrial production facilities and emissions. *n*-Hexane was added to the TRI process, with data available for an inventory baseline of 1996 (TRI96 1998).

Environmental Fate. *n*-Hexane is a highly volatile hydrocarbon and will partition to the atmosphere if released into surface waters or onto land surfaces. The fate of *n*-hexane in air is reasonably well described, with free radical degradation from hydroxyl radicals being of major importance. In water, biodegradation studies in surface water and groundwater are very limited, with most studies involving various petroleum fractions. Few studies were identified dealing explicitly with the fate of *n*-hexane in soils. Available studies (Heringa et al. 1961, Leahy and Colwell 1990, Rosenberg et al. 1992) indicate that *n*-hexane, along with other linear alkanes, is readily biodegraded under aerobic conditions. In soils near the surface, *n*-hexane's high volatility will usually result in its rapid transfer to the atmosphere. Given the volatility of *n*-hexane and its ready biodegradation under aerobic conditions, the most important data needed would involve degradation processes in groundwater, especially under anoxic conditions. Further research is needed to identify the rates of any relevant abiotic decay and transformation mechanisms (e.g., hydrolysis). These kinds of studies are important because they provide information about the movement or fundamental mechanisms of destruction of *n*-hexane in the environment and aid in understanding the behavior of *n*-hexane at hazardous waste sites.

Bioavailability from Environmental Media. Inhalation studies of humans indicate that *n*-hexane is bioavailable from the atmosphere. Although *n*-hexane in water or soil is likely to undergo transport to the air because of its volatility (although this would not necessarily be the case with *n*-hexane in groundwater), pharmacokinetic absorption studies using the oral and dermal routes of exposure would help clarify the bioavailability of *n*-hexane from water, soil, plant material, and other environmental media.

Food Chain Bioaccumulation. The physical constants for *n*-hexane (high volatility) and a low estimated BCF value for a typical fathead minnow forage fish (ASTER 1995) suggest that *n*-hexane will not concentrate significantly in aquatic organisms. No empirical information is available concerning BCFs for particular species or concerning the bioaccumulation or biomagnification of *n*-hexane in environmental media other than water. Information concerning the accumulation of *n*-hexane in several trophic levels would be useful in estimating human dietary intake; however, little intake is expected.

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Exposure Levels in Environmental Media. Some environmental monitoring data are available for *n*-hexane in air, while very limited data are available for drinking water, surface water, groundwater, and foodstuffs. Available data for air provide a very uneven coverage for background ambient settings, and recent investigations for contexts associated with commuter traffic or workplace settings are very sparse. The data for water are not sufficient to accurately characterize the concentrations present in drinking water, surface water, and groundwater. Virtually no data are available for soils. These data would be helpful in determining the environmental concentrations of *n*-hexane so that exposure of the general population as well as of terrestrial and aquatic organisms could be estimated.

Reliable monitoring data for the levels of *n*-hexane in contaminated media at hazardous waste sites are needed so that the information obtained on levels of *n*-hexane in the environment can be used in combination with the known body burdens of *n*-hexane to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites.

Exposure Levels in Humans. The database for *n*-hexane exposure levels in humans is limited to a few older detections of *n*-hexane in breast milk and determinations of levels in body fluids and alveolar air collected in foreign countries. A more current and complete database would be helpful in determining the current exposure levels, thereby permitting the estimation of the average daily dose associated with various scenarios (e.g., living near a hazardous waste site). Since *n*-hexane is rapidly metabolized within the human body, further studies correlating levels in the environment with the levels of metabolites and biomarkers in humans would be helpful. This information is necessary for assessing the need to conduct health studies on these populations.

Exposures of Children. Better documentation of the types of household products that still contain *n*-hexane would be extremely valuable since inhalation of vapors from such products in poorly ventilated interior rooms could pose exposure risks to children. Additional studies on *n*-hexane concentrations in breast milk are important to validate the findings from PBPK modeling discussed in Chapter 2.

Exposure Registries. *n*-Hexane is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry. *n*-Hexane will be considered in the future when chemical selections are 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 related to exposures.

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5.8.2 Ongoing Studies

Few studies dealing with opportunities for human exposure related to *n*-hexane were located in the literature. One set of ongoing studies under Dr. Charlene Bayer at the Georgia Institute of Technology (Bayer 1995) is examining metabolic gases from certain common fungi found in ductwork, crawl spaces, or the interiors of houses and office buildings. These metabolic gases can contain a variety of VOCs, including *n*-hexane. Exposure to these VOCs may play a role in the commonly designated "sick building syndrome."

As part of the Third National Health and Nutrition Evaluation Survey (NHANES III), the Environmental Health Laboratory Sciences Division of the National Center for Environmental Health, Centers for Disease Control and Prevention, will be analyzing human blood samples for *n*-hexane and other volatile organic compounds. These data will give an indication of the frequency of occurrence and background levels of these compounds in the general population.